

# SAFETY IN THE CHEMICAL LABORATORY

DR H. A. J. PIETERS

*Head of the Chemical Works Safety Department  
of the Netherlands State Mines*

with the collaboration of

DR J. W. CREYGHTON

*Head of the Medical Department of the  
Joint Netherlands Coal Mines*



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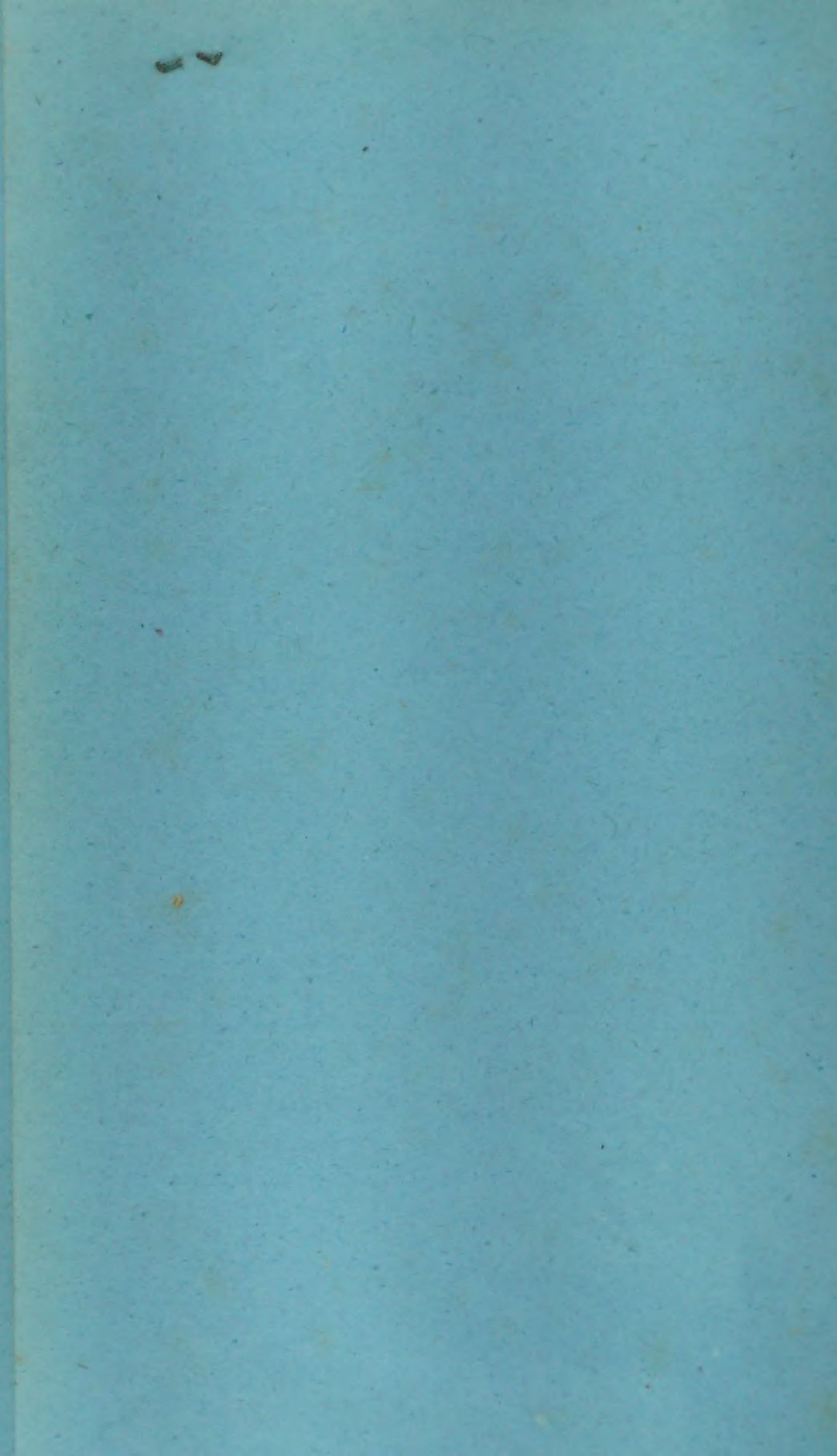
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SAFETY IN THE  
CHEMICAL LABORATORY

DEDICATED TO THE MEMORY OF  
DR D. P. ROSS VAN LENNEP



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## PREFACE

IN 1930 Dr H. A. J. PIETERS, the then Director of the Central Laboratories of the Staatsmijnen in Limburg, prepared a booklet issued by the Staatsmijnen for the instruction of employees in the chemical laboratories. Each member of the staff received a copy.

In 1942 and again in 1947 the original material was rewritten and enlarged with the cooperation of J. W. CREYGHTON, Chief Medical Officer of the Joint Coal Mines of the Netherlands. The 1947 edition, based on the experience gained and incorporating improvements arising from constructive criticisms of users, formed a complete text embracing all aspects of safety in chemistry.

When the opportunity arose to prepare an English version, the text was completely rewritten and brought up to date, with the object of making the book a basic international safety manual.

We hope that the collaboration of chemist and physician has produced a book which will prove helpful to all concerned with chemical operations, and trust the work will fulfil its purpose as a handbook and guide to students and to the staffs of chemical laboratories, helping them to protect themselves and their fellow workers against the potential hazards connected with their work, by showing how these can be combated successfully by taking precautionary measures and using appropriate equipment. These safety measures, together with the rudiments of first aid in case of accidents, and general outlines of the principles of careful and safe practice and accident prevention will be found in this book. It is intended primarily for laboratory assistants and students, but the inclusion of analytical methods and some tables of data should ensure that the book is useful to all chemists and to managements in the chemical industry in general.

To attain the object of promoting safety in the laboratory we emphasize that the book is primarily intended to be the property of every member of the laboratory staff. *It should be used on the laboratory bench, not in the library.*

In choosing the material for this book, we started from the observation that in a laboratory safe working conditions are not realized merely by issuing rules and regulations. The laboratory worker should acquire a safe style of working based on a general understanding of and a respect for the hazards involved. Consequently the principles underlying the hazards and the pre-

cautionary measures have been emphasized. In treating the hazards connected with the handling of chemicals, gases and dusts, the necessity for outlining the principles of physiology became evident, and special reference is made to the respiratory process and the way in which the harmful substance penetrates into the organism to exercise its toxic effect.

Safety appliances are described and a compilation of safety rules and regulations is given from which the laboratory director can make appropriate selection.

The last chapters of the book describe a series of analytical procedures for detection and estimation of contaminating substances in the air. These methods are those used in the Staats-mijnen laboratories where they have proved their usefulness and reliability. Several of these methods have been developed there and many others have been improved. Tests concerning flammable gases, and methods by which harmful substances can be detected or determined in blood and in organic matter, are included. The basic principles of dust sampling and analysis are outlined.

Extensive lists of references have been added to each chapter as an aid to the reader who wants further information.

On the one hand the book aims at educating the reader in the principles of working safely in the laboratory: on the other hand, circumstances will arise in which the reader needs direct information on a specific subject. This will be found in the tables at the end in which a wide range of numerical data has been summarized.

Naturally, in compiling this book many and various sources have been of great help. The most important have been enumerated in the references and in the list of manuals we consulted. The authors wish to express their thanks for the assistance rendered by Messrs W. R. J. BERKX and P. H. HERMANS in the preparation of the manuscript and in reading the proofs. The cooperation and the care bestowed by the publisher are beyond all praise. The authors are also greatly indebted to Mr ALEC WEBSTER for reading the manuscript and proofs and for making valuable suggestions.

We conclude with the traditional assertion that we are far from pretending to have exhausted all aspects of safety and accident prevention in the laboratory. The field of safety, even within the relatively narrow limits of this book, repeatedly enters adjacent fields of technical science. Hence it is most difficult to draw the line between what falls within and outside the scope of accident prevention techniques, and limits are apt to be arbitrary. For instance, in connection with the detection and determination of



toxic substances in the laboratory atmosphere, it has been necessary to impose rigid limitations so that the reader should be offered a carefully selected choice of methods of proved reliability. Consequently we have not aimed at completeness. Nevertheless we hope we have succeeded in offering a book in which every worker in the chemical laboratory and many a one working in an allied field of technical science may find useful hints, giving him the assurance that he is working in a safe place if he lives up to his responsibility. To management it offers advice in organizing the laboratory operations so that a maximum of safety can actually be achieved. Both quality and effectiveness of the laboratory work will benefit.

Although it will always remain impossible to eliminate every hazard, it makes all the difference when laboratory staff become safety-minded and acquire a correct appreciation of the dangers. University, college and school laboratories can contribute much to promote this ideal by including safety training in their curricula. Safety in the long run is never expensive ; it promotes efficiency and economy.

H. A. J. PIETERS

J. W. CREYGHTON

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Figures 6, 7, 8, 9, 10, 11, 16, 17, 18. From L. DAUTREBANDE *Les gaz toxiques* (1933) Masson & Cie, Paris VI

Figure 15 From L. DAUTREBANDE, *Standards Techn. Paper No. 212* U.S. Government Printing Office, Washington

Figure 19 From *Public Health Bulletin No. 272*

Figure 20 Messrs Siebe, Gorman & Co. Ltd. Salvus apparatus

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Figure 25 GODBERT, A. L. and WHEELER, R. V. *Safety in Mines Research Board Paper No. 56*



## CHAPTER 1

# GENERAL SAFETY CONSIDERATIONS

**T**HE most important factors in accident prevention are proper design of buildings and apparatus, good training and constant supervision of staff, and a general knowledge among all workers of the hazards and dangers and of the principles involved in preventing accidents and protecting the worker.

In all instruction to personnel, of whatever rank, it should be strongly impressed that all persons are responsible for the safety of the people whose work they control, and they should quickly and firmly correct any tendency to unsafe working.

Generally it will be found that written procedures, quoted as Instructions, are the best safeguard against accidents that are likely to occur *e.g.* for cleaning up spilt acids or alkalis. The responsibility for laboratory safety lies both with director and assistants. Everyone working in a laboratory should feel responsible for his own safety and that of his fellow workers. Regulations and advice may be helpful, but a sense of responsibility is essential.

Certain measures are of great value in promoting general safety. To be effective the laboratory assistants should understand their significance.

Adequate formulation and display of safety rules should be provided. Proper maintenance should be given to general and individual safety devices, such as ventilators, fire fighting equipment, first aid supplies, gas masks, safety goggles, and protective clothing. Regular inspection is of the greatest importance.

Safety instructions should be practised. Instructions and training help the staff to become familiar with the use of safety appliances.

Before assistants are started on a new task they should realize the potential dangers and take precautionary measures. Directions should be given in writing and discussed with the assistant. The director of the laboratory should satisfy himself periodically that all members of his staff know the safety instructions and act accordingly. The training of the laboratory staff is an essential factor in promoting safety in the laboratory. Safety rules should become an integral part of laboratory practice, and there must be adequate supervision and control to ensure that they are observed. The most

## GENERAL SAFETY CONSIDERATIONS

suitable place for recording safety instructions is in laboratory method books ; these instructions should not be left to the end but inserted in the appropriate place as part of the instructions.

Special attention should be given to cleanliness, tidiness, storage and transport of materials, electrical installation and equipment, fire prevention and fire fighting, and the handling of poisonous gases and chemicals. Negligence by staff should be penalized.

Each person must be responsible for the care of his own safety equipment, but responsibility for complying with the statutory requirements under the Factories Acts 1937 and 1948 for regular inspection of equipment rests with the laboratory director.

Laboratory staff should be taught to plan experimental work in advance, to understand the procedure thoroughly, to concentrate on the task in hand, to have adequate safety devices readily available, and, in an emergency, to act promptly. Unsafe conditions must be reported immediately.

### RESPONSIBILITIES OF THE DIRECTOR OF THE LABORATORY

**Storage**—Good and safe storerooms for glassware and chemicals must be provided. Glass tubes should be kept on racks and fragile apparatus stored so as to minimize the danger of breakage. The storeroom for chemicals should be well ventilated and directly connected with the open. Chemicals which might react together should be stored in different places. Volatile chemicals should be stored in a cool room away from heating coils and protected from direct sunlight. Strong acids and ammonia should be kept in a separate room provided with a powerful ventilator. Inflammable materials are preferably stored outside the laboratory in a room provided with automatic sprinklers and non-sparking lamps.

**Transport**—The transport of chemicals and glassware is always one of the main sources of accidents. It requires careful planning and a reliable organization.

**Training in technique**—Good technique is most important in the laboratory. Full attention must be given to the selection and training of all members of the staff. Neatness, order, cleanliness and careful planning should be practised always. It is dangerous to economize on safety devices. Full use must be made of them. The laboratory should be provided with an ample supply of fire extinguishers and all rooms should be well ventilated and lighted. Waste containers must be emptied daily. Spilled chemicals should be cleaned up and removed immediately.

**Instructions and regulations**—Every member of the staff should become safety minded through adequate training and repeated



## GUIDANCE FOR LABORATORY ASSISTANTS

practice. It is essential that every newcomer should receive training in safety practice before he is entrusted with the laboratory work proper. This also applies to all assistants who are transferred to other work. Instructions and training must include general precautionary measures as well as those which have been devised as a result of accidents.

Every accident is a lesson from which we can and must learn how to work safely. Instruction and understanding are most important. Regulations should be restricted to a minimum ; they are of little use unless instruction enables the worker to assimilate the sense of the regulation, and his active interest and cooperation have been obtained. Sometimes regulations serve to establish the responsibility for a fault or an accident.

**Medical inspection**—Medical examinations are advisable at regular intervals, preferably twice a year, for members of the staff who regularly work with poisonous chemicals.

## GUIDANCE FOR LABORATORY ASSISTANTS

In a laboratory, assistants have to handle fragile apparatus, inflammable, explosive and poisonous materials, and electric current. Operations at high and low temperatures and high and low pressures are common practice. Prevention of accidents in the laboratory, therefore, is not simple. Nowhere is there such a variety of operations being conducted in the same building, operations the outcome of which may often be wholly or partly unknown. As GROENEVELD<sup>1</sup> points out, minor accidents such as small fires or explosions are of quite frequent occurrence in laboratories, often with little or no personal injury. The safety programme, therefore, has to be restricted to general principles.

It is up to each individual laboratory worker to prevent accidents and to help in making the laboratory a safe place to work in. Since the intellectual standard of the laboratory worker is high, reliable safety devices are numerous, and the principles of safe working are well known, adequate training will ensure that safety becomes, as it were, second nature. A good laboratory assistant acquires such a feeling for safe working that, notwithstanding the many potential dangers, there should be no safer place to work in than the laboratory.

**General precautionary measures**—Laboratory work is connected with specific dangers. If this is properly borne in mind, as well as the measures which can be taken to safeguard one's self and one's colleagues, the chance of accidents happening is very slight. It must never be forgotten that carelessness or negligence may harm the operator and others. Everyone should aim consciously at safe

## GENERAL SAFETY CONSIDERATIONS

working, should avoid carelessness or recklessness, and should keep his whole mind on what he is doing, with due feeling of responsibility for safety. Orderliness and cleanliness are of the utmost importance : clean glassware, adequately built apparatus, and a clean and orderly bench are essential for successful laboratory work.

In routine operations exhaustive safety precautions can be devised. There is a serious danger, however, that continued practice will make the worker so familiar with the work that the possible dangers are no longer evident and safety instructions tend to be disregarded. All workers must be continually on their guard against such an attitude of mind.

When working with materials the properties of which are unknown or insufficiently known, it is wise to begin with such small amounts of the chemicals that major accidents are out of the question. Reactions and reagents must always be considered in the light of safety and apparatus devised accordingly.

Care must be taken to avoid reactions which may proceed violently *e.g.* bumping during a distillation when no pumice has been added to the liquid, or when pumice has been added to the hot liquid. When working with large quantities of chemicals, too rapid heating must be avoided and a reaction component must never be added in large portions. Water leaking into a hot oil bath or into a reaction vessel through a badly connected cooling tube or a cracked flask has been the cause of serious accidents.

**Typical safety precautions**—In a laboratory the assistants regularly handle glass apparatus which is liable to fracture, causing injury by broken glass fragments and possibly by the contents of the apparatus. It is always wise to consider the consequences in the event of the apparatus breaking, and to guard against such happenings by taking measures to minimize the consequences.

The dangers involved in working with gas and with electric currents should be familiar. All electrical apparatus should be tested and safely mounted, preferably by an expert, while modifications and repairs should be made according to safety rules.

Special safety measures should be taken in handling high or low pressures.

Apparatus is not the only source of danger : the various chemicals handled in a laboratory may be injurious to health. Such chemicals require special precautions. The physiological action is known for a great many substances but not for all. It is wise to treat all chemicals as poisonous.

Operations involving special dangers should be carried out in a separate room, where special precautions can be taken. Dangerous chemicals should not be kept in quantities in the laboratory rooms



## BIBLIOGRAPHY

but should be safely stored under lock and key. Readily inflammable materials should be stored in a fireproof building isolated from the main buildings.

When carrying out operations involving the evolution of poisonous gases or dust, care should be taken to work in an efficient draught cupboard, or to have the experiments performed in the open. When such general precautions are impracticable or insufficient, individual safety devices such as goggles, shields, masks, or protective clothing must be used. All laboratory workers should be prepared to assume responsibility for the safety of those under their care, and should at all times carry out all laboratory procedures rigidly and without any deviation from instructions.

### GENERAL CONSIDERATIONS

Remember that being too careful is better than being reckless.

Consider beforehand the consequences should apparatus break, take fire, or develop pressure or vacuum.

Many substances reveal their poisonous nature only after a long interval.

Accident occurrence is not governed by the law of averages.

Accidents are not the inevitable price of progress. Caution is never something unworthy ; recklessness has nothing to do with courage.

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## CHAPTER 2

# PRECAUTIONS WITH GLASSWARE, PLATINUM, GAS AND ELECTRICITY

### GLASSWARE

**G**LASS is fragile and may break suddenly on account of internal strain. This strain may be already present in the apparatus owing to wrong or inadequate heat treatment during manufacture, but it can also be the result of unsuitable or inadequate mounting of the apparatus. When handling or cleaning glassware care must be taken to avoid scratching it.

A flask, beaker or bottle may break through local overheating *e.g.* with a non-luminous flame, the inner cone of which is touching the bottom of the flask. Thick-walled bottles and measuring flasks should never be heated. For this reason solutions should never be made in a bottle, a measuring cylinder or a washing bottle as the heat of the solution may cause the container to break. This is illustrated by a typical accident quoted by GROENEVELD<sup>1</sup>.

A chemist's assistant had to prepare a concentrated solution of sodium hydroxide. For this reason she put solid sodium hydroxide in a bottle (first mistake) and added the required amount of water. Then she closed the bottle (second mistake) and shook it, holding the bottle on a level with her eyes (third mistake). The heat of solution created a considerable pressure in the bottle. The bottle broke and the hot, concentrated solution splashed over the face and eyes of the victim. The result: total blindness.

Every laboratory assistant must be taught that sodium hydroxide should be dissolved in an open beaker or flask of heat resistant glass, the liquid being stirred with a glass stirrer. Even such a simple manipulation as the preparation of a solution of sodium hydroxide can cause a fatal accident.

Even when mistakes are avoided, glassware can break accidentally. Steps must therefore be taken to minimize the dangers resulting from breakage. Vacuum desiccators, Woulff bottles, Dewar flasks, apparatus for vacuum distillations *etc* should be provided with mantles of metal gauze, since such apparatus can break quite unexpectedly. After a vacuum distillation the vacuum should never be released until the flask has cooled down to room temperature.



## HANDLING PLATINUM

Distillation apparatus, especially when handling inflammable liquids, should be placed in a flat metal tray. If breakage occurs and a fire is caused the burning liquid will not spread over the table or floor, and can be extinguished more easily. The floor of the tray is best covered with sand and a small scoop provided for spreading the sand over the fire.

When the formation of noxious or irritating gases is to be expected, the apparatus must be set up under a hood.

Every laboratory assistant should be trained in the elementary manipulation of glass, such as cutting a glass tube, inserting and removing a tube or thermometer into and from a cork or rubber stopper, drawing out and bending a glass tube. When a glass blower's workshop is at hand it is an advantage to set up apparatus with the glassblower's assistance.

## HANDLING PLATINUM

Although incorrect handling of platinum apparatus is not dangerous it can constitute a heavy burden on the laboratory budget. The inclusion of notes on the proper care of this material is therefore considered justifiable<sup>2,3,4</sup>.

**Substances with detrimental effect on platinum**—Various substances have a detrimental effect on platinum. Minute quantities (a few tenths of a milligram) are quite sufficient to destroy a platinum crucible or dish.

Substances causing damage are :

- a* most metals, the more so at higher temperatures : they combine with the platinum to form alloys with a relatively low melting point, leading to punctures in the crucible or dish
- b* many metal compounds such as the easily reducible metal oxides and salts of heavy metals : when heated in a platinum crucible they may be reduced to the metal by organic substances (filter paper) and the flame
- c* hydrogen, which diffuses rapidly through glowing platinum, causing pitting. The blue core of a burner flame should never impinge directly on to platinum
- d* silica, phosphorus and arsenic: these cause intercrystalline corrosion. Even very small amounts of phosphorus are destructive. This accounts for the rapid deterioration of platinum crucibles used for the incineration of organic substances containing phosphorus, and in the determination of magnesium and phosphates.

Over 80 per cent of platinum crucibles which have to be renewed have been damaged by phosphorus.

Platinum is attacked by many other elements and chemicals, especially by free chlorine (aqua regia, hydrochloric acid with an oxidizing substance) and alkali metal hydroxides, carbonates, sulphides, cyanides and thiocyanates which have an appreciable effect on platinum at high temperatures.

Table 57, p 244 gives a more complete survey. The influence of carbon and reducing flame gases and of sulphur and gases containing sulphur appears to be relatively unimportant.

Platinum objects should be cleaned with molten potassium hydrogen sulphate and then polished. Mechanical damage should be avoided.

**Regulations for handling platinum objects**—Platinum crucibles should never be used when roasting or incinerating phosphates and other phosphorus compounds if reduction is not completely excluded. Contact between platinum and metal triangles, tongs and water baths must be avoided : ivory or chamois leather tipped tongs should be used.

Easily reducible metal compounds (oxides, salts of heavy metals such as lead, silver, tin, antimony, bismuth, copper) or arsenic compounds must not be heated in a platinum crucible or dish.

The platinum should not be exposed to sudden changes in temperature ; this may produce cracks. It should be cleaned with molten potassium hydrogen sulphate, the melt being removed after cooling by immersion in boiling water. Mechanical damage may be avoided by using the wooden core.

Fixed melts should not be removed by adding a solvent and putting the crucible on a water bath, or by heating the crucible until the surface of the mass begins to melt. The crucible should be allowed to cool, a little water added and the whole heated for a short time. The melt can be loosened by swirling the crucible during cooling. The melt may also be removed by re-melting, inserting a platinum wire in the mass, and allowing it to solidify again. When the platinum wire is drawn out, if necessary after gently heating until the outside of the mass begins to melt, the mass can easily be removed.

By alloying the platinum with a certain metal (ruthenium, niobium, tantalum, osmium) the material can be made resistant to many chemicals, including phosphorus and arsenic.

## FUEL GAS

Most fuel gases are poisonous and leaks must therefore be avoided. It is advisable that there should be an easily accessible mains gas tap for every individual room of a laboratory organization, so that the gas can be turned off for the whole room in the event of a leakage.



The non-luminous flame of a bunsen or a meker burner is difficult to see in daylight. Therefore a lighted burner should not be placed near the edge of a table, and a burner which is not in use should be turned off.

Mixtures of gas with air or oxygen are self-combustible and often explosive. The explosion of a mixture of gas and air may have serious consequences.

Before closing the laboratory, it should be checked that all gas cocks are turned off. A rubber tube may burst or slip off, and the escaping gas form a combustible or even explosive mixture which can be ignited, for instance, by electrical apparatus. Therefore, when leaving the laboratory it is desirable to switch off all electrical apparatus, except such heating and drying apparatus as are flame and sparkproof.

If the smell of gas is detected in a room, a match should never be lighted, but ample ventilation immediately provided by opening doors and windows, and the gas cocks should be checked. Leakages should be detected by the smell or by means of a soap solution ; never with a flame! Before igniting the gas or heating an apparatus through which gas is flowing one should wait until air has been displaced completely and check by collecting a sample of the gas in a test tube to see if it is explosive. As soon as the test is found negative the gas can safely be ignited. The same precautions should be taken when a gas meter is used, in order to avoid accidents caused by an explosive mixture of gas and air.

When operating gas heated apparatus (ovens, distillation apparatus) a pilot flame should be lighted before turning on the main gas supply. Apparatus which may contain an explosive gas should be protected by a mantle of metal gauze and kept in a place where no flame is burning, all gas cocks should be turned off and smoking should be prohibited.

There are further dangers involved in working with gas. When gas flames are burning in a small or unventilated room the oxygen content of the atmosphere may become too low and the carbon dioxide and moisture content too high, which is detrimental to health. Moreover, by incomplete combustion of the gas the very toxic carbon monoxide is formed in considerable quantity. This may be expected when the flame has flashed down the burner, or is improperly adjusted, or when the non-luminous flame touches a cool object such as a large beaker or a kettle filled with cold water, and consequently is cooled below the ignition temperature of the products of the primary combustion reaction. A well adjusted flame burns with a blue inner cone, which should not touch the object to be heated.

Sometimes a combustible gas or an explosive mixture of gas and air can be formed inside a reaction vessel heated by a flame. When there is a crack in the glass the mixture can be ignited.

### ELECTRICAL HAZARDS

Electrical equipment may give rise on the one hand to fires and explosions and on the other hand may cause personal injury and even electrocution. Static electricity is a common source of unexpected fires and explosions in handling non-conducting combustible liquids and combustible materials in general.

**Electric shock**—Live conductors present a definite hazard. The body may be regarded as a sensitive ammeter the resistance of which varies with circumstances and with the individual. It responds even to very small electric currents, the effect of AC being more serious. With 60 cycles AC the threshold of perception has an average value of 1.0 ma. The let-go current is 6 to 9 ma. Above this value the current causes such a violent contraction of the muscles that the victim cannot release his grip. At 25 ma breathing becomes difficult or impossible, causing asphyxiation resulting in respiratory paralysis. In such cases the patient can be saved by immediate and continued artificial respiration.

At 100 ma the heart is affected by ventricular fibrillation which is nearly always fatal. Currents of 1 amp and more cause severe burns. These data are summarized in Table 1.

Supposing the area of the surface of the contacts is 100 cm<sup>2</sup> and the resistance 5,000 ohms, a voltage of 5,000 volts will produce a current of 1 amp. The heat developed per second is  $0.24 I^2 RT = 1,200$  cal or 600 cal per contact per sec, or 2,160 kcal per hour per cm<sup>2</sup>, or 216,000 kcal per hour per m<sup>2</sup>.

Table 1. Effect of Electric Shock<sup>5</sup>

Effect	Current ma		
	AC 50 c/s	AC 60 c/s	DC
Threshold of perception through skin	1	1	5
Threshold of muscular decontrol : let-go current ... ..	15	6-9	70
Threshold of danger to life from failure of heart and respiration ...	20	25	80
Threshold of fibrillation ... ..	100	100	100



## ELECTRICAL HAZARDS

The danger increases with increasing frequency of the generator, the body acting as a condenser, but very high frequencies are safe. With DC the threshold current is 5 ma and the let-go current 40 to 60 ma.

The resistance of the body may vary according to circumstances from 100 to 500,000 ohms. FLAMMACHE describes a series of experiments in which the resistance was 100,000 ohms when the man touched both electrodes with one dry finger each.

With moistened fingers the resistance dropped to 40,000 ohms and when moistened with a salt solution to 16,000 ohms. When the electrodes were gripped in the hands the resistance fell to 1,200 ohms and with both hands immersed in the salt solution to 700 ohms.

Assuming that a current of 50 ma is usually fatal, the fatal voltage is 5,000 v when the resistance is 100,000 ohms ; 220 v corresponding to a current of 2.2 ma which produces a shock only.

When circumstances are unfavourable the resistance is much lower, say for example 20,000 ohms. Then 220 v AC produces a current of 11 ma which already exceeds the let-go current.

Because of the many variables in contacts with live conductors, electrical equipment must always be treated with respect. Electrical apparatus which produces the slightest shock presents a potential danger and must be disconnected and checked over immediately. Damaged flex and connections are dangerous. Patched flex should never be used adjacent to earthed objects and moisture enhances the hazard of live conductors (damp basements, tanks, bathrooms). Before making repairs or alterations to electrical equipment the current should always be switched off and fuses drawn. Electrical hot plates should not be covered with asbestos because this will favour local overheating.

Some electrical apparatus may be designed so that the current is cut off automatically when the door or lid is opened, as in Figure 1, where opening the furnace lid interrupts the current.

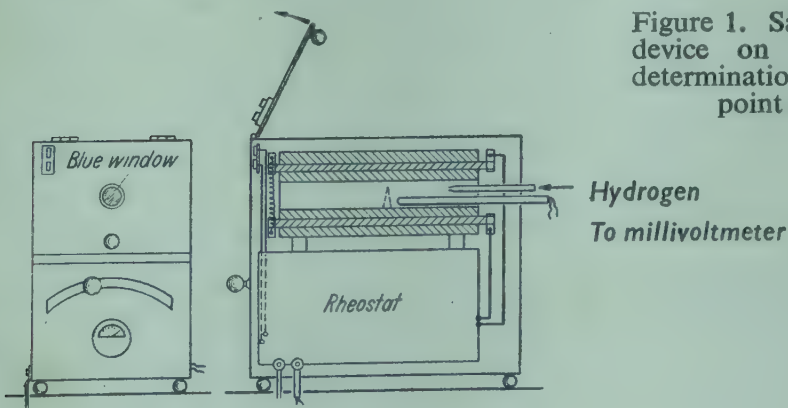


Figure 1. Safety opening device on furnace for determination of fusion point of ash.

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## CHAPTER 3

# FIRE HAZARDS

**L**ABORATORY employees are liable to receive burns caused by burners that have blown back, hot glass, non-luminous flames, ignition of inflammable solvents, or clothing catching alight.

Burns are far from innocuous. They cause severe pain, loss of lymph, and poisoning by the absorption into the blood of toxic products from decomposition of the burning substance and the body tissues. They may give rise to infections and to the formation of scars.

Combustible materials are frequently used in the laboratory, involving fire risks against which the worker can and must protect himself and the laboratory. Some of the principal precautionary measures will be indicated in order to assist the worker to acquire such insight as will enable him to take prompt and appropriate action in an emergency.

Regular inspection of all electrical installations, apparatus and wiring is necessary to ensure that they are safe and reliable. Rubber gas connecting tubes must be watched to prevent slipping or splitting of a tube.

Tidiness is most important. Accumulation of materials in lockers and corners, near machinery, steam pipes, boilers, furnaces and stoves should be avoided. Waste should be kept in metal containers with self-closing covers. Rubbish should be burned in the open in a convenient place, at a safe distance from the building.

A fire is an exothermic reaction, mostly between an oxidizable substance and oxygen. It is started by a local rise in temperature. As soon as the temperature exceeds a certain value, which depends on several circumstances, the reaction proceeds spontaneously with increasing velocity. This temperature, when measured under standardized conditions, is specific for the combustible material and is called its ignition temperature. Substances with a low ignition temperature should be handled with care.

**Spontaneous ignition**—It is essential to remember, however, that most oxidation reactions are already proceeding below the ignition temperature with a definite, though small, velocity. As long as the conditions are such that the heat of combustion is eliminated so

rapidly that it does not produce a rise of temperature, the reaction will continue to proceed slowly and nothing serious will happen. If, however, the heat is allowed to accumulate *e.g.* where there is sufficient air for the oxidation but not enough ventilation to carry the heat away as fast as it is generated, the temperature rises steadily. This causes the reaction to proceed faster, more heat is developed, and finally a fire is started. In principle every combustible material is liable to such spontaneous ignition in the presence of air or oxygen. A large surface exposed to the air without adequate air circulation and the presence of some moisture is a favourable condition for spontaneous combustion. Well known examples are the spontaneous combustion of hay, coal, drying oils, pyrites, sawdust and waste materials. Many fires are the result of the spontaneous ignition of oil-soaked or paint-saturated rags and waste. Such material should be deposited in covered metal receptacles provided for this purpose and emptied daily. Storage of combustible materials near a heated wall, stove or chimney, the presence of a catalyst, an increase in the concentration of oxygen, and a decrease in the loss of heat to the environment by insulation, all increase the fire risk.

The ignition temperature indicates whether under specified circumstances a combustible material can be ignited more or less easily. The heat of combustion of the material gives an idea of the probable magnitude of the fire. The heat conductivity of the material (Table 28, p 204) is one of the factors determining the loss of heat to the environment, substances with a low heat conductivity being more liable to accumulate the heat of a slow oxidation reaction.

Some substances and mixtures are self-combustible. This means that no additional oxygen is necessary for burning because the substance contains sufficient oxygen to produce an exothermic oxidation reaction once the reaction has been started *e.g.* by a local rise in temperature. Striking examples are provided by many organic nitrates and nitrocompounds, thermite and gunpowder.

Combustible materials such as wood and fabrics can be fireproofed by treating them with chemicals such as ammonium phosphate, waterglass and alum. This treatment lowers the inflammability but does not alter the combustibility.

When fighting a fire it must be borne in mind that a fire consumes oxygen and generally produces noxious combustion products such as carbon dioxide, sulphur dioxide, oxides of nitrogen and carbon monoxide. Therefore self-contained breathing apparatus should be available for fire brigades.

**Sources of ignition**—The combustible material may be ignited by an unprotected flame, an incandescent surface, discarded cigarette stubs, frictional heat, sparking tools, electrical equipment, motors,



## PARTICULARLY DANGEROUS SUBSTANCES

switches, batteries, lamps, the switching off of a current, static electricity, a chemical reaction. A round flask filled with water when placed on a wooden bench in direct sunlight will act as a magnifying glass and thereby can start a fire. A relatively slight increase in the oxygen concentration of the air causes the combustion reaction to proceed with greater speed and violence. For this reason it must be remembered that handling oxygen cylinders means increased fire risk *e.g.* for clothes. Various opinions are held about the advisability or otherwise of smoking in laboratories and it is safer to forbid it. There is always the possibility of accident because of flames being set up by lighted cigarette ends and there is the additional danger that cigarettes smoked while the fingers are chemically stained may cause ingestion of poison into the system.

In many processes static electricity is a typical source of fire. It is produced by moving parts of machinery and in extraction, grinding, painting and drying processes. The hazard of static electricity is greatest in dry, cold weather. The flow of a non-conducting liquid through pipes and the transference of such a liquid into another container may create sufficient static electricity to cause a spark and thereby start a fire. Therefore, receptacles into which any appreciable quantity of inflammable liquid is to be poured should be adequately grounded, as well as the units from which the liquid is to flow.

By using electrically conducting rubber *i.e.* in conveyor belts, flooring and petrol hose, the dispersal of static electricity can be promoted. The rubber can be made conducting by incorporating special types of graphite and carbon blacks. As rubber is generally regarded as an electrical insulator the articles made of conducting rubber should be marked so as to avoid hazards<sup>1</sup>.

## PARTICULARLY DANGEROUS SUBSTANCES

With some substances and combinations of substances fire hazard is particularly great. The following are some typical examples :

### SOLIDS

Filter paper soaked with nitrophenol deposited in a waste bin can give rise to an unexpected explosion.

Mixtures of oxidizing substances such as ammonium nitrate or potassium chlorate and organic matter are self-combustible. They should be handled with great care and never deposited in the normal waste bin.

The following frequently occurring combinations cause an increased fire hazard :

*a* active carbon with ammonium nitrate

## FIRE HAZARDS

- b* rags soiled with paint or with a drying oil. Because of the large surface and the heat insulating capacity of the rags, as well as of the exothermic polymerization and oxidation reactions of the oil, conditions are favourable for the accumulation of the heat of reaction resulting in self-ignition. Such waste should be deposited in closed metal containers
- c* laboratory clothing soiled with oxidizing substances such as potassium chlorate
- d* rags with concentrated sulphuric acid
- e* combustible materials (wood, fabrics) with concentrated nitric acid
- f* liquid air or oxygen and organic matter
- g* aluminium with chlorinated organic compounds *e.g.* aluminium powder with chloroform.

**Routine precautions**—Care must be taken that residues of combustible materials do not get into the sewer, waste pipes, or the waste bin. A laboratory fire has been started by the spontaneous combustion of zinc powder deposited in a waste bin. In England there is a statutory power, given under the Petroleum (Consolidation) Act, 1928, for local authorities to make by-laws for the storage and treatment of certain inflammable liquids. These by-laws usually include a clause making it obligatory to take steps to prevent liquids or vapours getting into public sewers.

Some substances catch fire immediately on coming into contact with the air *e.g.* phosphine, pyrophoric metal powders, silicon hydride, metalalkyls and white phosphorus. The latter should for that reason be kept in a bottle completely filled with water and closed with a ground stopper. Such bottles should be placed in a metal container or in a basin filled with water in a frost-proof room. Phosphorus is slightly soluble in water (0.0003 per cent at 20°C) and certain gaseous products are formed. Minute particles become detached from the greater lumps or sticks and are oxidized slowly, acidifying the covering water. At higher temperatures the solubility increases, causing a more rapid acidification. This process will in time corrode a metal container at the liquid level. When the acidity becomes higher than 0.5 per cent the water should be neutralized with soda or lime but not made strongly alkaline because this would favour the formation of phosphine ; *pH* 9 is a safe limit.

## LIQUIDS

Combustible liquids are widely used in the laboratory. They present special fire and explosion hazards.

It must be borne in mind that it is the vapour of the liquid which catches fire or, when mixed with air, causes an explosion. The vapour



pressure, and therefore the concentration of the vapour in the air at room temperature, is specific for the substance ; it increases rapidly with temperature.

**Flash point**—The lowest temperature at which the liquid gives off vapour near the surface in sufficient quantity to form an inflammable mixture with the air is called the flash point of a liquid combustible. When the temperature of the liquid is below its flash point it will not catch fire when a small flame is applied to it. Therefore the lower the flash point the more likely that the liquid will be set on fire by a flame, spark or a hot surface.

The addition of a substance with a low flash point increases the fire hazard of a liquid *e.g.* petrol in fuel oil. Once in the gaseous state, or as a fine mist or spray, the combustible substance is very inflammable.

Methods for the determination of flash points have been standardized in England by the Institute of Petroleum and are published by them in their book *Standard Methods for Testing Petroleum and its Products*.

For liquids having a very low flash point REINDERS' method is available : the temperature of the liquid is gradually raised and occasionally a spark is generated near the surface of the liquid. The flash point is defined as the lowest temperature at which a minor explosion takes place.

**Ignition temperature**—The ignition of the liquid is the lowest temperature at which the vapour on coming into contact with the air will ignite spontaneously.

**Explosive limits**—If the concentration of the vapour in the air is within certain limits the combustion proceeds with such speed and violence that it causes an explosion. The explosive limits are the minimum and maximum concentrations of the vapour in air beyond which propagation of the flame does not occur when the mixture is in contact with a source of ignition. The mixtures within the explosive limits constitute the explosive range. This is generally a comparatively narrow band in the zone of low concentrations. For this reason an empty flask or drum which has contained an inflammable liquid is more dangerous than if full, the emptied container being more apt to be filled with an explosive mixture of vapour and air.

Instructions for the storage and transportation of inflammable liquids distinguish three classes characterized by the liquid's flash point (see Table 30, p 206).

**Extraction and distillation**—Most laboratory fires arise from extractions and distillations with inflammable solvents such as ether, alcohol, benzene and petroleum ether. They have become such routine operations that their fire hazard is apt to be forgotten.

The most efficacious means of preventing such fires is to see that the inflammable liquid and its vapour cannot come into contact with an unprotected flame or a glowing object. Electrical heating, steam and hot water baths and safety burners can be helpful for minimizing the risk. Electrically heated apparatus is not quite fireproof, since the vapours can be ignited at the glowing surface of the elements. Safety burners are unreliable because the flame is often insufficiently protected.

In operations with inflammable liquids having a low boiling point *e.g.* carbon disulphide, ether, acetone and low boiling petroleum fractions, steam heating should be applied. For inflammable liquids of medium boiling point, such as benzene, toluene, xylene, medium petroleum fractions, alcohol, and amyl acetate, the use of a safety burner or a water bath is permitted, provided that the cover of tightly woven metal gauze which surrounds the flame is undamaged and clean and the lid shuts well. This last point should be checked regularly. The flame should be adjusted so that it remains always within the gauze. The cover does not give protection when the flame has flashed back.

Oil baths are also hazardous. The oil may contain water or water may get into the hot oil, or the oil vapours may be ignited. After continued use the flash point of the oil decreases. Aluminium blocks are safer and also more convenient ; electrically heated jackets fitting the flask are even better. There is, however, the disadvantage with these electrically heated jackets that should the heated flask crack or break the hot solvent will seep through the heated jacket and come into contact with the hot wire element, when fire or explosion may follow.

If possible, operations with inflammable liquids should be performed in a fireproof room or under a specially provided hood. In distilling inflammable liquids it is most important to prevent bumping and local superheating by never filling the flask more than half full, adding fresh pumice before heating, and heating slowly and gradually. The flask should not be refilled while it is hot or near a flame, and pumice should never be added to the hot liquid. Copper or chromium nickel steel distillation flasks are safer than glass apparatus. The flame and flask should be protected by a metal screen which ensures more efficient use of the flame and avoids local overheating.

A weak point is the connection between flask and distillation column, especially when the temperature is high, which may cause the cork or rubber stopper to be decomposed by the heat or by the vapours, with the result that the vapours escape into the air and may catch fire. The stopper may be protected with asbestos or waterglass.



Whenever possible it is better to use a standard ground glass connection. If lubrication is necessary the lubricant should be sufficiently inert to preclude chemical action with the substances being distilled, with consequent heating.



Figure 2. Device to control flow of water through a cooler.

Before starting a distillation it is well, as a matter of routine, to check that the cooling water is circulating *e.g.* with the aid of the small reservoir illustrated in Figure 2. Should a fire start its results can be minimized if precautions have been taken in setting up the apparatus for distillation and extraction in trays of enamelled iron or of aluminium containing a layer of sand. Bottles or cans containing inflammable liquids should be kept in a fireproof room outside the laboratory buildings. Burners and hot plates should not be placed directly on the bench but on a piece of fireproof material. The greatest care must be taken not to spill inflammable liquids.

**Disposal of inflammable liquids**—There is a serious danger involved in careless handling of inflammable liquids. If these get into the drainage system they may give rise to the formation of inflammable or explosive mixtures, as illustrated by the following example<sup>2</sup>.

An explosion which occurred in a sewer on the premises of an examination hall in 1932 resulted in much material damage and injury to two students and was caused by a winchester quart of waste carbon disulphide being poured down a drain, with repeated flushing with water. Apparently this method of disposing of accumulated waste carbon disulphide had been customary for some months, since complaints of odour had been made as a result of pouring the waste on to land at the back of the building.

Carbon disulphide is a very dangerous substance. It is poisonous, endothermic, and can be detonated by shock. It has a very low flash point and a very high vapour pressure. Mixed with air or oxygen it forms a violently explosive mixture which can be fired by flame or shock. Catalytic agents, such as iron rust, or even surfaces in the right physical condition, may start the reaction.

The Acts and Regulations relating to the discharge of materials into sewers or connecting drains are very numerous. Generally no chemical or manufacturing refuse, or any substance dangerous to the health of persons entering the sewer or injurious to the structure of the sewer, may be discharged into the sewer.



The disposal of carbon disulphide is rather difficult and if possible it should be recovered. It is very convenient to use it as fuel for burning waste material but it should be remembered that its vapour is extremely toxic and therefore it should not be allowed to evaporate indiscriminately into the air.

The hazards caused by carbon disulphide are also illustrated by the following accidents which occurred in the author's laboratory practice.

After an extraction with carbon disulphide using an electrically heated sand bath placed in a hood, spontaneous combustion occurred several hours after the extraction was completed. On another occasion a chemist had thrown an extraction thimble into the waste bin. Some time afterwards his colleague deposited a hot test tube into the bin, thereby causing an explosion.

Most inflammable vapours, being heavier than air, will flow along the benches and can be ignited by a flame burning at an apparently safe distance, so when such liquids are being distilled the use of naked flames should be avoided. No smoking should be permitted. Flames of matches often cause accidents, as for instance<sup>3</sup> when someone used a lighted match to look into a drum. As a result an explosion which seriously injured two persons occurred. The reader is likely to say that such a thing will not happen to him : however, in the same month the following accident occurred in another laboratory.

After emptying a wooden drum containing a suspension of an organic substance someone was careless enough to use a match to see if the drum was empty, although a special control lamp was available for the purpose. The flame of the match caused an explosion and a flash burst forth from the opening of the vessel. Thanks to his spectacles the man's eyes were saved, but his face was severely burned.

The following accident<sup>4</sup> is also very instructive as it illustrates on the one hand how a combination of circumstances can have most tragic consequences and on the other hand that human behaviour is not always governed by reason.

A laboratory employee had in his hand a small beaker with benzene with which he was cleaning a flask. A draught from an open window carried the benzene fumes to the open flame of a distillation apparatus about five feet away. The flame flashed back to the beaker, causing the employee to throw the beaker away, spilling the burning contents over his face and body. Before the flames could be extinguished with a fire blanket the injured man had swallowed enough flame to cause death 30 hours later.

**FIRE EXTINGUISHING**

Self-combustible materials have only to be ignited to burn out completely *e.g.* explosives, incendiary mixtures, thermite, and mixtures of organic compounds and an oxidant. Such reactions, when started, are very difficult to stop. Normal fires, however, are kept burning only by a sufficient supply of oxygen. They can be extinguished

*a* by removing or shutting off the fuel supply

*b* by shutting off the air supply

*c* by cooling below the ignition point.

When a container filled with a combustible liquid such as oil, alcohol or benzene catches fire the fire can often be extinguished by covering the container with a lid, thereby shutting off the air. Some types of fire extinguishers have a similar action, isolating the burning material from the air ; this so-called smothering action or blanketing effect is of special importance on fires of inflammable liquids.

For this reason sand, salt, sodium bicarbonate mixed with sawdust, or sodium and calcium carbonate, may be used to advantage on materials which prohibit the use of water. They should be located within easy reach and should be poured carefully over the fire at close range.

**Types of extinguisher**—The carbon dioxide extinguisher is especially useful in the laboratory. It is very effective in putting out a small fire and has the great advantage that it does no harm whatsoever to the apparatus and can be used in the presence of live electrical apparatus. The laboratory should be amply provided with carbon dioxide extinguishers. They are easy to handle and can be refilled. As carbon dioxide has practically no cooling effect the fire may start anew as long as the temperature of the combustible material remains above the ignition temperature. A foam extinguisher can be most useful for extinguishing burning liquids. The stable foam covers the liquid and isolates it from the air. Since it is a good conductor, foam should not be used in connection with fires of an electrical nature.

Liquid halogenated hydrocarbons are widely used in fire extinguishers. The liquid, when sprayed on a burning material, forms a heavy inert vapour which acts as a blanketing agent. The halogen moreover has a specific effect in suppressing the combustion. Because they are non-conducting they can be used in or near electrical equipment. Carbon tetrachloride and methyl bromide are commonly used in this type of extinguisher. Although their extinguishing effect is very satisfactory they have the major disadvantage that they are highly toxic. In the fire they are decomposed to soot and hydrogen



chloride, sometimes with formation of phosgene which is extremely poisonous.

Carbon tetrachloride and similar types of extinguishing agents should therefore only be used in the open or in well ventilated rooms. Carbon tetrachloride must never be used on a fire involving alkali or alkaline earth metals, with which it gives an explosive reaction. It is claimed that chlorobromomethane is several times as effective as other agents. Its fire extinguishing properties are believed to be due to the presence of the bromine atom<sup>5</sup>. A recent American report has shown, however, that chlorobromomethane is no less toxic than carbon tetrachloride, and also that most of these chlorinated compounds tend to decompose on heating to produce toxic compounds.

Water has excellent fire fighting properties because of its high specific heat and heat of evaporation. It has, however, many disadvantages. In the first place it damages apparatus and laboratory furniture. It cannot be used with burning liquids that float on water, as the water then promotes the spreading of the burning liquid. Moreover it may be dangerous to aim a jet of water at electrical apparatus.

In the laboratory it occasionally happens that the chemist's clothes catch fire. To meet this emergency each laboratory should be provided with one or more showers and fire blankets. By rolling the victim in a blanket the fire can be quickly smothered. A stream of carbon dioxide from a fire extinguisher, not aimed at the victim's face, can also be used for this purpose.

All members of staff should be periodically instructed and trained in the use of fire extinguishers and the fundamentals of fire fighting. These extinguishers and other fire fighting equipment should be properly maintained and frequently inspected, so that they are constantly in operating condition and free from corrosion.

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## CHAPTER 4

### EXPLOSION HAZARD

**S**OME exothermic reactions involving gaseous or finely dispersed components or reaction products may proceed with explosive speed and violence. With mixtures the reaction velocity depends on the composition and reaches a maximum value for a definite composition.

The explosive limits as well as the curve indicating the reaction velocity as a function of the composition of the mixture are influenced by a great many factors such as pressure, temperature, presence of catalysts, the dimensions and material of the vessel, and direction of propagation of the flame.

Self-combustible substances and mixtures, such as explosives, are naturally liable to explosions. Many unstable endothermic compounds may decompose causing a violent exothermic reaction *e.g.* acetylene. The utmost care is needed in working with acetylene even at comparatively low pressures and temperatures<sup>1</sup>. Ethylene at a temperature above 350°C at a pressure of approximately 175 kg/cm<sup>2</sup> (170 atm) decomposes with explosive violence<sup>2</sup>.

Most substances of this type are characterized by certain atom groups *viz* :

O—O	ozone, peroxide
O—Cl	chlorate, perchlorate
N—Cl	chloride of nitrogen
N=O	in organic compounds
N=N	diazo compounds, azides
N—C	fulminate
C≡C	acetylene

Some typical examples of explosive reactions which may occur in normal laboratory routine will be treated in more detail.

### ETHER EXPLOSIONS

Ether has a high vapour pressure at room temperature, a low flash point and a low ignition temperature. Mixtures of ether vapour and air or oxygen are explosive within a wide range. Air containing one gram of ether vapour per litre is self-combustible : the ignition temperature is 180°C. When working with ether a flame must never

be used; a steam bath should be used instead. Ether vapour has a high specific gravity (the vapour is 2.6 times heavier than air) so that vapour leaking from a bottle or from apparatus will spread over benches and floors and may be ignited by a flame at a relatively great distance.

Ether easily forms peroxides which are very explosive. For this reason distilling water-free ether always involves the risk of dangerous explosions. During the distillation the peroxide accumulates until in the end it may cause a violent explosion. The following are typical examples.

A violent explosion occurred during the distillation of ether supplied as chemically pure quality. The distillation was carried out in a water bath. Towards the end of the distillation an oily residue was left which exploded at a temperature below 100°C. The splinters of glass flew through the room and destroyed the whole of the other glassware<sup>3</sup>.

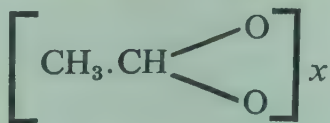
Thick glass vessels have been seen to be neatly punctured at several yards distance as a result of flying splinters from a thin-walled distillation flask<sup>4</sup>. In fat determinations, after the greater part of the ether has been driven off in a water bath, the ether extract is heated for another hour at 105°C. During such a determination an explosion occurred which destroyed the drying oven, one person being wounded by glass splinters<sup>5</sup>.

In ethyl ether supplied as chemically pure, HETZEL<sup>6</sup> detected ether peroxide. After he had used this ether for a fat extraction and the ether had been evaporated, he wished to dry the residue (fat + peroxide) at 105°C. A violent explosion occurred.

WILLIAMS<sup>4</sup> has proved that peroxides are also formed in ethers other than diethyl ether *e.g.* in diisopropylether. Other substances such as dioxane<sup>7</sup> and unsaturated hydrocarbons *e.g.* butadiene, may cause violent explosions as a result of the formation of peroxides.

**Peroxide formation**—Peroxide is formed by the autoxidation of ether in the presence of oxygen or ozone. The reaction is favoured by ultraviolet rays and especially by the presence of acetaldehyde<sup>7</sup> which acts as oxygen carrier or as sensitizer. One mol of oxygen is added.

Another substance of similar explosive character is ethylidene peroxide<sup>9</sup>.



Usually the peroxide has a higher boiling point than the compound from which it is formed; hence explosions are likely to take place



towards the end of a recovery distillation. It is customary to add an inhibitor to prevent spontaneous oxidation of the ether during storage. WILLIAMS<sup>4</sup> recommends 1- or 2-naphthol, hydroquinone or diphenylamine in 5 per cent concentration. Active carbon or active aluminium oxide should be added to ether which is shipped or stored. It should be pointed out that an inhibitor will prevent the formation of a peroxide but will not destroy any which has already been produced. It is, therefore, essential that such peroxide forming bodies are tested for the presence of peroxide immediately before distillation and if this is found it should be destroyed before any distillation takes place.

**Precautions with ether**—The explosion hazard connected with the storage of ether may be prevented by keeping the ether in contact with active carbon or with active aluminium oxide. It is recommended that water should be added to the ether.

Before using ether it should be checked whether it contains peroxide, even when the ether need not be evaporated completely. Distilling ether to one tenth of its initial volume involves risk of explosion. Moreover the peroxide as a strong oxidizing agent may cause undesired reactions. If the ether contains peroxide this should be destroyed by adding an acidified 2N ferrous sulphate solution<sup>8</sup>. Sometimes this reaction proceeds so violently that the ether begins to boil. After a few minutes no more peroxide is present. Now the ether contains the decomposition products of peroxide, acetaldehyde and acetic acid : in order to remove these it is shaken with a solution of chromic acid and then with sodium hydroxide solution until the liquid reacts alkaline. Subsequently the ether is distilled over sodium carbonate.

In Williamson's method the ether is shaken with 1 per cent potassium permanganate powder and 1 per cent potassium hydroxide solid and allowed to stand for some days, after which the ether is distilled off.

#### EXPLOSIVE MIXTURE OF ETHER AND AIR

The explosion at \*Ludwigshafen on 28 July 1948 was probably caused by the ignition of a mixture of dimethyl ether and air. The ether was stored in a tank painted dark, parked near a wall which radiated heat on an abnormally hot day. The tank burst, the ether spread over a considerable area, and was ignited by an open fire<sup>9</sup>.

#### POTENTIALLY EXPLOSIVE SUBSTANCES

Oxidizing compounds in contact with organic substances are apt to cause explosions. Great care is necessary in handling concentrated nitric acid, hydrogen peroxide, chlorates, nitrates, persulphates and especially perchloric acid.

**Perchloric acid**—This may react explosively with reducing agents and organic compounds. Moreover the anhydrous acid may explode spontaneously. Combustible materials which have been soaked with aqueous perchloric acid and dried may be ignited by impact, friction or heat. The dangerous anhydrous acid is produced from the salts or from aqueous solutions by heating with high boiling acids. The explosions are extremely violent and destructive. Discoloured acid should be discarded by pouring into cold water and flushing. The 60 to 70 per cent acid is stable and can be stored safely. At concentrations above 85 per cent the acid is liable to spontaneous explosion. The commercial acid can be boiled safely at atmospheric pressure if concentrated to a constant boiling mixture containing 72.4 per cent  $\text{HClO}_4$ .

Magnesium perchlorate, which is used as a drying agent, is stable but should not be used in the presence of a strong acid or of organic matter. Serious explosions have resulted from using magnesium perchlorate for drying an organic liquid which had been in contact with sulphuric acid and had been poorly washed.

Esters of perchloric acid are also violently explosive. An alcoholic solution of perchloric acid should never be heated unless considerable water is present, nor should it ever be evaporated.

Perchloric acid<sup>10</sup> must always be considered as a most dangerous substance which may give rise to unexpected, always violent, explosions, especially during evaporations and particularly in the presence of organic matter *e.g.* in alcohol determination of potassium.

When the concentrated acid or its vapour comes into contact with an organic or with an oxidizable matter serious explosions may result. Tongs must always be used to manipulate a crucible or a dish with perchloric acid and good ventilation is essential when evaporating it. The vapours of perchloric acid attack wood and make it easily ignitable; floors and flues should be tiled and made of fireproof material and frequently flushed with water. With ammonia or with nitric acid the condensed vapour of perchloric acid will form explosive mixtures.

**Cobalt nitrate**—Explosions of cobalt nitrate have been explained on the basis of the fact that mixtures of nitric and nitrous acids with certain organic compounds are liable to produce fulminic acid and ethyl nitrolic acid, both of which may become explosive. This reaction is accelerated by the presence of traces of heavy metals.

**Potassium permanganate**—An explosion occurred<sup>11</sup> when concentrated sulphuric acid was mixed with crystalline potassium permanganate in a vessel which was drained but not dried.  $\text{Mn}_2\text{O}_7$  is explosive at 70°C.



**Benzoyl peroxide**—The following interesting accident has been described<sup>12</sup>.

The accident occurred when a screw-stoppered bottle containing benzoyl peroxide was opened. Probably the bottle had been left open in a dusty atmosphere and the mixture of benzoyl peroxide and organic dust which had collected in the threads of the stopper detonated when the bottle was opened.

The crystallization of benzoyl peroxide from hot chloroform is liable to cause explosions.

It is best to avoid the heating by adding methanol to the chloroform solution at room temperature<sup>13</sup>.

**Ammonium nitrate**—This is a powerful oxidant so that mixtures of ammonium nitrate and an organic substance are particularly dangerous. Above 160°C ammonium nitrate decomposes exothermically, producing gaseous products.

**Dangerous mixtures**—The following substances or combinations may cause explosions :

- a* perchloric acid with alcohol
- b* sodium or potassium with water ; aluminium powder with ammonium persulphate and water
- c* a chlorate with antimony sulphide
- d* *idem* with phosphorus or a cyanide
- e* chromium trioxide or potassium permanganate with sulphuric acid, sulphur, glycerol, or organic matter
- f* organic matter and aluminium (alloys) in nitrate-nitrite salt baths
- g* ammonium nitrate with zinc powder and a drop of water
- h* barium rhodanide with sodium nitrate
- i* potassium nitrate with sodium acetate
- j* nitric acid with thiophene, or with hydrogen iodide
- k* nitrate with an ester
- l* nitrite with potassium cyanide
- m* peroxides with magnesium, zinc or aluminium
- n* chlorates and perchlorates with sulphuric acids
- o* nitric acid with zinc, magnesium or other metals
- p* potassium ferricyanide, mercuricyanide, halogen with ammonia
- q* phosphorus with nitric acid, nitrate, chlorate
- r* mercuric oxide with sulphur
- s* magnesium and aluminium with chlorate or nitrate
- t* nitrate with stannous chloride
- u* magnesium with phosphate, sulphate, carbonate and many oxides



## POTENTIALLY EXPLOSIVE SUBSTANCES

v oxalates of heavy metals

w liquid air or oxygen with organic matter (liquid nitrogen is preferable as a cooling agent).

Concentrated formic acid is unstable and may explode. Carbides, particularly those of copper and silver, are very explosive. From ammoniacal silver solutions highly explosive compounds may precipitate ; such solutions should never be stored.

Liquid ammonia and mercury *e.g.* from manometers, may form an explosive compound.

**Precautions**—When working with hazardous substances it is advisable to observe the following principles:

Only small quantities of such chemicals (not more than 100 mg) should be used. Heating should take place on a water bath, not in a flame.

Such compounds should not be kept and residues must be destroyed.

A screen of transparent splinterproof material should be used. Figure 3 shows a shattered screen which took the full force of an explosion. Figure 4 shows protective screens for various types of apparatus : desiccators, Woulff flasks, distilling and suction flasks, screens for general use, safety burners.

**Destroying dangerous residues**—Halogen nitrogen compounds are destroyed by making alkaline with ammonia, azides and silver fulminate by acidifying, diazo-compounds by boiling with water

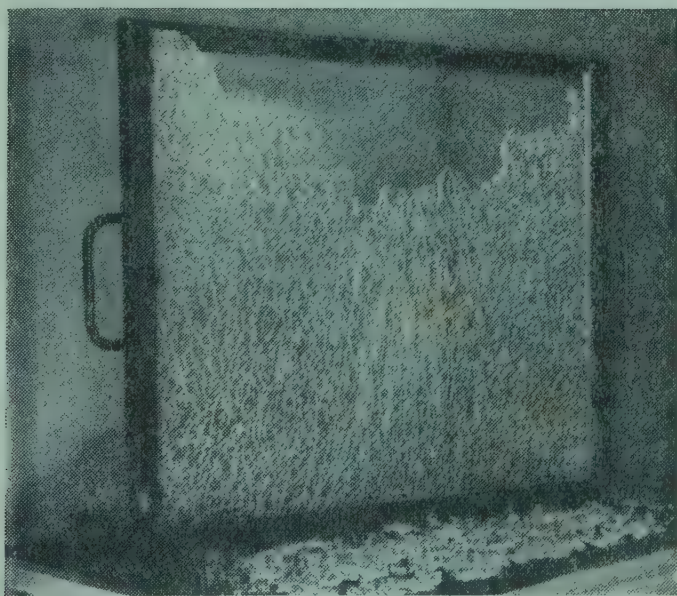


Figure 3. Transparent screen of splinterproof material shattered by an explosion.

## EXPLOSION HAZARD

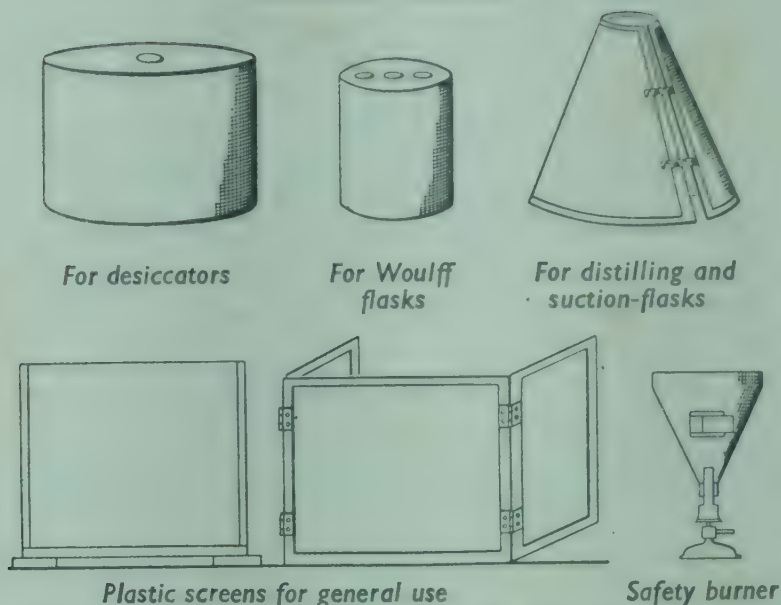


Figure 4. Protective screens of fine metal gauze or plastic.

acetylides by decomposing with ammonium sulphide, and peroxides by reduction.

**Dust explosions**—A dust explosion is caused by the rapid combustion of a cloud of dust in the air, when the heat is generated much faster than it is dissipated to the surroundings. It is similar to a gas explosion and characterized by a sudden development of pressure. Explosive dust clouds can be formed by any combustible material in finely divided form, when the cloud is sufficiently dense and there is a suitable source of ignition (spark, breaking of a lamp, heated surface, open flame, gas explosion).

The principal factors governing the explosivity of a dust cloud are the ease of oxidation and the heat of combustion of the dust and the oxygen requirements.

Some powders may be pyrophoric. The minimum concentration for a dust cloud to be explosive is of the order of 20 mg per litre of air for many organic dusts. The explosivity can be diminished by the admixture of inert dust.

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## CHAPTER 5

# CYLINDERS CONTAINING COMPRESSED GASES

**C**YLINDERS of compressed gases must be handled with care. They should not be dropped or thrown and should be fastened securely *e.g.* with a fine chain, to the bench. They should be protected from all sources of heat and from direct sunlight to prevent increase in pressure, especially when they contain dissolved or liquefied gases, such as acetylene, ammonia, chlorine, sulphur dioxide, carbon dioxide. Table 2 gives the increase of pressure of a cylinder of carbon dioxide with temperature.

Table 2. Pressure/Temperature relations in a carbon dioxide cylinder

<i>Temperature</i> <i>t° C</i>	<i>Pressure</i> <i>p kg/cm<sup>2</sup></i>	<i>Temperature</i> <i>t° C</i>	<i>Pressure</i> <i>p kg/cm<sup>2</sup></i>
0	36	20	74
5	40	34	80
15	52	45	140

Excessive cooling should also be avoided, because steel becomes brittle at low temperatures.

Most accidents with cylinders are due to careless handling. Other factors are internal and external corrosion, changes which may take place in the material through rough handling, strains caused by welding, and the rapid decrease of the toughness of the material at low temperatures.

The head of the cylinder is especially liable to damage so that during storage and transport it should be protected by the valve-protecting cap. During storage the cylinders must be protected against moisture and heat as well as against all damage likely to affect the mechanical properties of the cylinders.

Cylinders should be properly marked so that no doubt can arise as to their contents *e.g.* by painting on the name and formula of the gas contained. In addition a coloured band may be painted on the cylinder, characterizing its contents (Tables 50, 51, pp 234, 235). The colours have not been standardized internationally. International agreement would be helpful.



**Identification of gas cylinders**—In the United States each cylinder or manifolded gas supply unit is stencilled, stamped or labelled with the chemical or trade name of the gas. These markings must not be cut into the metal of the cylinder.

Cylinders filled with inflammable gases carry a red label, non-inflammable gases a green label, extremely dangerous poisons a white poison-gas label, and acids a white acid label.

§ The extremely poisonous gases are: chlorpicrin, cyanogen, diphosgene, ethyldichlorarsine, hydrocyanic acid, lewisite, methyl-dichlorarsine, mustard gas, nitrogen peroxide (tetroxide), phenyl-carbylmonochloride and phosgene (diphosgene).

Colours are not used to identify the gas content of cylinders for the following reasons :

- a* There are literally hundreds of gases and combinations of gases. Any attempt to use a separate colour or combination of colours to identify each gas would lead to confusion and mistakes
- b* compressed gas cylinders receive hard service that may damage, discolour or conceal the paint
- c* a considerable percentage of human beings are colour blind and cannot distinguish all the colours of the spectrum
- d* colours appear differently under some light sources, such as fluorescent and mercury vapour types of light
- e* some gas suppliers use cylinder colours that are different from those used for the same gas by other suppliers.

In Germany the name of the gas is cut into the metal of the cylinder.

Cylinders should never be used for or refilled with any other than the specified gas. Cylinders, for instance, which have been used for methane, coal gas, or any other combustible gas, always contain considerable quantities of inflammable material as condensate and residues of compressor oil. If such cylinders were to be refilled with oxygen, serious accidents might happen.

For the same reason every type of cylinder requires a special pressure reducing regulator with a pressure gauge and a safety valve, illustrated in Figure 5. Cylinder and regulator should be kept in good repair and should be examined regularly. It is dangerous to force them with large wrenches.

The different types and fittings of the regulators make interchange impossible, thus preventing the formation of mixtures which e.g. in the case of oxygen and an inflammable gas, would be very dangerous. For the same reason a cylinder should never be emptied completely, thus preventing air from entering the cylinder. The

# CYLINDERS CONTAINING COMPRESSED GASES

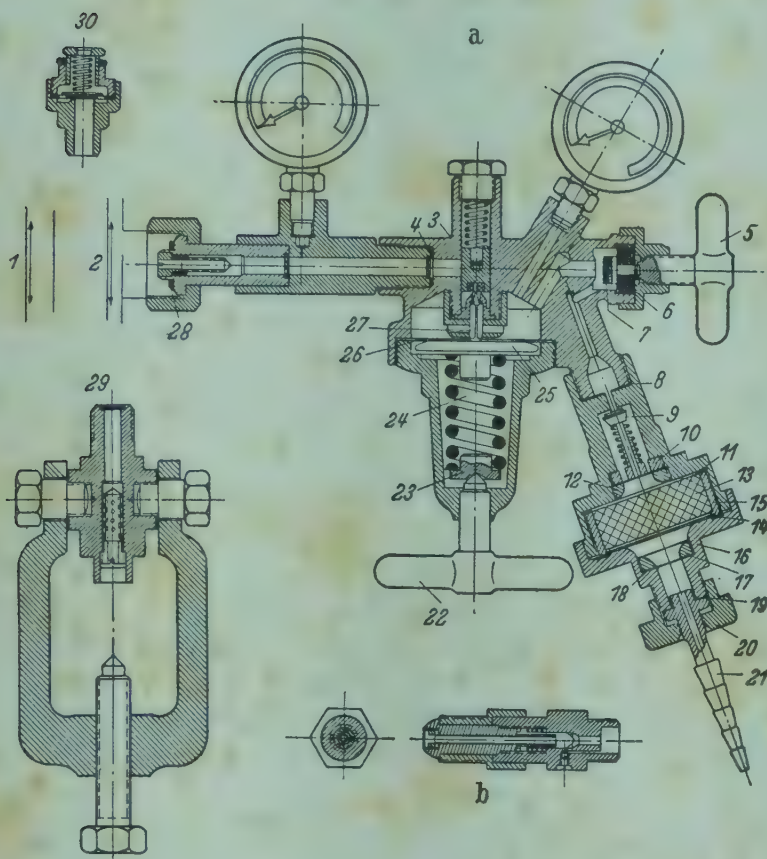


Figure 5. a Pressure regulator and safety valve for compressed gas cylinders, and b Wino apparatus.

- |  |                                      |
|--|--------------------------------------|
| 1 For oxygen cylinder, with right thread and Wino apparatus. | 16 Porous mass.                      |
| 2 For hydrogen cylinder with left thread and nipple.         | 17 Nut.                              |
| 3 Safety valve.  | 18 Sieve.                            |
| 4 Packing.   | 19 Fibre packing.                    |
| 5 Low pressure regulating screw.                             | 20 Cap nut.                          |
| 6 Rubber.  | 21 Nipple.                           |
| 7 Hard rubber.   | 22 High pressure regulating screw    |
| 8 Fibre packing.   | 23 Pressure disk.                    |
| 9 Valve.   | 24 Spring governor.                  |
| 10 Sieve.  | 25 Pressure disk.                    |
| 11 Rubber packing.   | 26 Membrane.                         |
| 12 Nut.  | 27 Regulating valve.                 |
| 13 Flash arrester.   | 28 Joint.                            |
| 14 Rubber packing.   | 29 Hoop bond for acetylene cylinder. |
| 15 Brass ring.   | 30 Safety valve.                     |



packing material must also be adapted to the nature of the gas ; rubber packing must not be used for chlorine cylinders.

After the cylinder has been installed and properly fastened the main valve should be opened for a short time to remove moisture or impurities which might otherwise get into the regulator. The regulator is then attached, the valve opened with the regulator closed and the outflow regulated by means of the regulator before connecting up with the apparatus.

When the work is finished, or before the laboratory is vacated, the tube should be disconnected from the pressure regulator, the valve of the cylinder closed, and the regulator emptied and closed.

Cylinders with chlorine, sulphur dioxide, carbon monoxide and ammonia should be kept in the open, because leaks are both unpleasant and dangerous.

**Oxygen cylinders**—In handling oxygen cylinders it must be remembered that oxygen in the presence of combustible materials causes fire hazards. Oil or grease, therefore, must never be used for the valve and pressure regulator of an oxygen cylinder. Jets of oxygen should never be allowed to strike oily or greasy clothes or the interior of a drum that has been used for inflammable substances.

The pressure regulator contains a small packing of hard rubber. When the valve is opened abruptly the heat generated by the rapidly augmenting pressure in the regulator can set the packing ring on fire, causing a small explosion and damaging the regulator. To prevent the pressure in the regulator from increasing suddenly when the valve is opened, the use of a special valve or the application of the Wino apparatus (Figure 5a) is recommended.

By opening the valve the oxygen can only enter the regulator through a narrow slit ; the main access to the regulator is shut off until the pressure in the regulator has reached its maximum value. The same mechanism shuts off the oxygen if for some reason the tube slips from the regulator and the pressure suddenly decreases.

Oxygen should never be used instead of air.

**Acetylene cylinders**—These should be protected from flash backs by an approved flame arrester.

Acetylene is a very dangerous substance. It is very inflammable, has a high heat of combustion, and being an endothermic compound is liable to exothermic spontaneous decomposition, which causes an additional hazard.

This decomposition is assisted both by increase of pressure and temperature. When dissolved in acetone it is relatively harmless. To prevent part of the dissolved gas from accumulating to form gas pockets the acetylene cylinder should be completely filled with a



porous, heat resistant material. Organic materials being liable to exothermic decomposition at a relatively low temperature should not be used for this purpose. The temperature of the acetylene cylinder must be prevented from rising as this causes high pressures and favours the decomposition of the acetylene.

The connection between valve and pressure regulator should not leak. Leaking gas is liable to ignite, and the burning gas will heat the cylinder. When an acetylene cylinder begins to feel warm, it is an indication that decomposition has started. The valve must be closed and the cylinder cooled immediately and not used again before it has been examined and tested.

The threshold pressure above which acetylene is liable to spontaneous explosive decomposition is  $1.4 \text{ kg/cm}^2$  at  $15^\circ\text{C}$ . A rise in temperature favours decomposition. Above  $300^\circ\text{C}$  it starts with an exothermic polymerization. From  $500^\circ\text{C}$  the acetylene begins to decompose exothermically.

The following specifications concern an acetylene cylinder such as is used for welding purposes.

The cylinder is filled with a porous mass, assumed to have 80 per cent porosity. The free space in the cylinder therefore amounts to 80 per cent of its bulk volume. A cylinder of 40 litres contains an average of 14.3 litres acetone. When acetone is compressed to a pressure of  $(15 + 1) \text{ kg/cm}^2$ , the volume of the solution of acetylene in the acetone has become 26 litres. The free space is thereby reduced  $32 - 26 = 6$  litres. The solubility of acetylene in 1 litre acetone at  $15^\circ\text{C}$  is 25 litres of  $1 \text{ kg/cm}^2$  and  $15^\circ\text{C}$ . The total quantity of acetylene in the cylinder therefore is  $16 \times 14.3 \times 25 \times 5,720$  litres at  $1 \text{ kg/cm}^2$  and  $15^\circ\text{C}$ .

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## CHAPTER 6

# PHYSIOLOGICAL EFFECTS OF CHEMICAL SUBSTANCES

WHEREVER materials are being handled substances may be dispersed in the surrounding atmosphere, especially when the material has an appreciable vapour pressure or when it is dispersed as mist or dust. Handling in closed systems, preferably under a vacuum, is the most effective means of preventing the dispersal of material. This method is generally only applicable in more or less permanent installations. Where the method cannot be applied we must face the hazards which may be connected with the dispersal of the materials we are using.

In the laboratory most chemicals handled daily constitute a potential health hazard. In order to guard against such hazards it is necessary to know how toxic substances enter the body and to gain a general appreciation of their effect on the human organism.

Toxic substances can enter the body with the air we breathe and with the food we eat. Some can penetrate the unprotected skin. Eating during work should be prohibited. Hands can be kept clean and inadvertent swallowing of caustic or toxic substances can be avoided, but we cannot avoid breathing, and breathing continuously. It will be obvious that the most likely mode of entry of a toxic substance in the body is with the air we breathe.

If the air is contaminated a large amount of the toxic or irritant substances will be inhaled in a relatively short time, especially during physical exercise. Hence the risk of absorption of a toxic substance by the respiratory tract is most important. For this reason the following treatment of the elementary principles of physiology will be restricted mainly to the respiration process and the principles of toxicology will be limited to those substances which may penetrate into the body as gas, mist or dust. In addition to describing the mode of entry, the transport of the harmful substance once it has entered the body will be discussed, including the effect it has on the organism in general and specific organs in particular. The knowledge thus acquired will form the basis of a correct appreciation of the precautionary measures which can and should be taken to prevent the hazards connected with our work in a laboratory.



**ELEMENTS OF PHYSIOLOGY AND RESPIRATION**

For its energy requirements the body depends on oxidation reactions and these imply a regular supply of oxygen, which is taken from the air and absorbed by the blood. The process, called respiration, takes place in the lungs, where the air is constantly refreshed by an intermittent increase and decrease of volume. The elastic lungs thereby follow the movements of the chest, which is intermittently enlarged and contracted by muscular activity.

The air passes through the nose, the trachea and the bronchi to the lungs. In the nose the air is conditioned as to temperature and humidity, dust and germs being partly filtered. The bronchi branch in the lungs to air tubes which in turn branch to finer tubes and so on. The mucous membrane of the air tubes is covered with cilia-bearing cells. By their rhythmic movements the cilia drive the secretion with the fine dust and germs towards the throat, where it is eliminated. The finest tubes end in clusters of microscopic air sacs or alveoli ; hence our lungs are completely filled with tubes and alveoli. The latter are enveloped by a network of minute capillaries through which blood circulates.

On one side the wall of the alveoli is in contact with air, on the other side with blood. Because the wall which separates the blood from the air is very thin and moist the oxygen can diffuse from the air into the blood, and gases dissolved in the blood can pass into the air. Thus a kind of dynamic equilibrium is established for every gas present in the blood or in the air, the direction of the gas flow being from higher to lower partial pressures. The difference in partial pressures determines the rate of transfer of a gas.

The lungs, being filled with the thin-walled alveoli and blood capillaries, are of necessity extremely vulnerable. They are therefore securely located in the chest, thus necessitating respiratory movements to ensure the ventilation of the lungs. The capacity of the blood to take up oxygen is enormously enlarged by the presence of haemoglobin, which acts as oxygen carrier. It is present in the red blood corpuscles and combines with oxygen, forming oxyhaemoglobin. In contact with the body tissues the reverse reaction takes place ; oxygen is consumed by the tissues in the oxidation processes which constitute their normal activity, the oxyhaemoglobin being reduced to haemoglobin.

Normal blood contains so many red corpuscles, from which it derives its typical colour, that the oxygen diffusing through the walls of the alveoli is absorbed immediately. Under normal conditions the blood takes up one fifth of its volume of oxygen, 2 per cent of which is dissolved in the blood plasma and 98 per cent combined with haemoglobin.

Table 3. Consumption of oxygen and removal of carbon dioxide according to Stelzner

Position	Frequency of inhalations per min	Volume inhaled in each breath		Exhalation		CO <sub>2</sub> delivery rate		O <sub>2</sub> consumption	
		litres	ft <sup>3</sup>	l/min	ft <sup>3</sup> /min	l/min	ft <sup>3</sup> /min	l/min	ft <sup>3</sup> /min
Lying ... ..	14	0.35	0.01	4.9	0.17	0.15	0.006	0.18	0.006
Sitting ... ..	18	0.40	0.01	7.2	0.25	0.21	0.008	0.25	0.0092
Walking— 85 paces per min ...	20	0.75	0.025	15	0.6	0.45	0.015	0.53	0.018
125 paces per min ...	23	1.4	0.048	32	1.1	0.70	0.025	0.90	0.032
185 paces per min ...	24	1.7	0.06	41	1.4	1.3	0.045	1.5	0.051
Walking upstairs— 111 steps per 80 sec ...	24	1.7	0.06	40	1.4	1.6	0.055	1.85	0.063
Running fast— 220 paces per min ...	40	2.05	0.07	82	2.8	2.4	0.082	2.7	0.092
Running upstairs— 111 steps per 28 sec ...	40	2.6	0.08	84	2.9	3.6	0.123	3.6	0.123



Because the oxygen is chemically combined with the haemoglobin the oxygen pressure of the saturated blood is relatively low, and the oxygen flows constantly from the air to the blood at a velocity which is determined by the pressure of the oxygen in the air present in the alveoli and indirectly by the oxygen pressure of the atmosphere.

In the living cells of the body oxidation reactions provide the cells with energy. In muscular activity a considerable quantity of this energy is liberated as heat, so that the body becomes warm by muscular exercise. The constituents of the cell act as the fuel which is consumed in the oxidation reactions. They are regularly regenerated from the nutrient constituents supplied by food. The heat evolved by the activity of the body is dissipated to the surroundings. This equilibrium is governed by sensitive regulators so that the temperature of the body normally remains constant.

**Oxygen-carbon dioxide equilibrium**—The combustion products of the respiration process are water and carbon dioxide. The carbon dioxide produced in the tissues is absorbed by the blood and removed in the lungs, because the air we normally inhale contains only a slight amount of carbon dioxide. Table 3 shows the variation of oxygen intake and carbon dioxide removal during different body activities.

In order to supply the body with the required amount of oxygen the inhaled air must contain a sufficient concentration of oxygen.

When the oxygen pressure of the inhaled air, which is normally 150 mm mercury, falls below 120 mm mercury the functions of the body are seriously impaired: this is especially dangerous as the body gives no warning. This figure represents an oxygen content of 16·7 per cent in the air, and should be regarded as the absolute minimum. It is better to consider an oxygen content of 19 per cent as being the limiting value for safe working. Numerous authorities quote figures higher than this.

Table 4. Variation of air intake with body requirements.

Circumstances	Heat energy kcal/ min	Oxygen required		Inhalation rate	
		l/min	ft <sup>3</sup> /min	l/min	ft <sup>3</sup> /min
Lying down ... ..	1·15	0·24	0·008	6	0·20
Sitting ... ..	1·44	0·30	0·010	7	0·24
Standing ... ..	1·72	0·36	0·012	8	0·27
Walking 2 mph (3 km/hr) ...	3·13	0·65	0·022	14	0·48
Walking 4 mph (6½ km/hr) ...	5·76	1·20	0·041	26	0·89
Running ... ..	9·60	2·00	0·068	43	1·47
Maximum exertion ... ..	14·20	3·4	0·11-0·14	65-90	2·3-3·2

By the respiratory movements the lungs are ventilated regularly with the result that the air in the alveoli, which is in contact with the blood capillaries, has a constant composition: under normal conditions 100 mm oxygen pressure and 40 mm carbon dioxide pressure.

The frequency and the depth of the respiration therefore have to vary between wide limits with our body exertions. The volume of air inhaled is automatically adapted to the oxygen demand of the body and may vary from about 10 to 100 litres per minute. The figures in Table 4 are related to the oxygen requirements of an average man, weighing 68 kg (10 stone 11 lb).

**Efficiency factors**—The efficiency of the respiration is determined by several factors as quoted by HENDERSON and HAGGARD<sup>1</sup>.

- a* The oxygen carrying capacity of the blood, which depends on the quantity of haemoglobin distributed over an average of five million red cells, with a diameter of  $7.5\mu$ . This corresponds to 14 to 17 gm per 100 ml of blood
- b* the surface area in the lungs where blood is in contact with the air. This surface is very large ( $120\text{ m}^2$ ) because of the great number of alveoli (of the order of 6 million), the total length of the blood capillaries (of the order of 3,000 km) and the surface of the red cells ( $2,500\text{ m}^2$ )
- c* the capacity of the lungs, which varies in different individuals and is seriously diminished in many lung diseases
- d* the intensity of breathing *i.e.* the combination of breathing movements (depth and frequency) and the velocity with which the blood circulates (maximal breathing capacity)
- e* the partial pressure of the oxygen in the air.

Alterations of the lung tissue, obstruction of air tubes, swelling of the tissues, or exudation of liquid into the alveoli, failure of the circulation and changes in the composition of the blood decrease the respiratory capacity.

In the capillaries surrounding the tissues the blood gives up oxygen, *via* the liquid in which the tissues are embedded, to the cells by the dissociation of the oxyhaemoglobin. In this way the oxygen requirement of the cells is automatically and constantly satisfied. The carbon dioxide produced in the tissues is absorbed in the blood and for the greater part converted into bicarbonate ions. The equilibrium between carbon dioxide and bicarbonate keeps the *pH* of the blood constant. In the lungs the carbon dioxide passes from the blood to the air in the alveoli.

**Oxygen-haemoglobin equilibrium**—The equilibrium between haemoglobin and oxygen is determined by the dissociation curve represented in Figures 6 and 7.



Table 5. Partial pressures of oxygen and carbon dioxide in the body and in the atmosphere

	<i>Atmosphere</i> mm Hg	<i>Alveolar air</i> mm Hg	<i>Tissues</i> mm Hg
<i>Oxygen</i> ... ..	150	100	40
<i>Carbon dioxide</i> ...	<i>very low</i>	40	50

The dissociation curve shows that above an oxygen pressure of 100 mm mercury the saturation of the haemoglobin is approximately ninety per cent. As soon as the oxygen pressure falls below 80 mm the oxyhaemoglobin dissociates.

The carbon dioxide content of the blood influences the dissociation equilibrium of the oxyhaemoglobin. The low carbon dioxide pressure in the alveoli promotes the formation of oxyhaemoglobin. The high carbon dioxide pressure in the tissues promotes its dissociation (Figure 8). Figure 9, p 44, illustrates this point.

**Regulation of respiration**—Respiration has to be automatically regulated so that it supplies exactly the amount of oxygen consumed by the oxidation reactions in the body and at the same time completely removes the carbon dioxide which is produced. The amounts of energy, oxygen and carbon dioxide involved in the process are proportional. The respiratory centre which governs the respiratory motions is extremely sensitive to the slightest change in the carbon dioxide content of the blood. Thus the respiration is accurately and immediately adapted to the oxygen requirement and the energy consumption of the body.

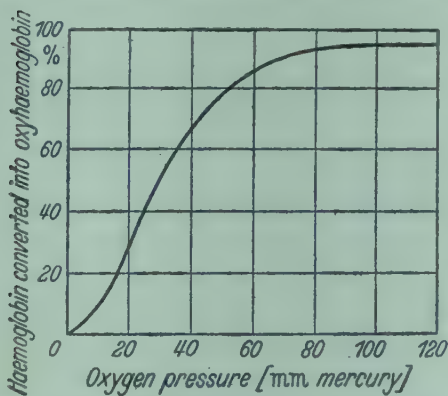


Figure 6. Dissociation curve for oxyhaemoglobin, according to DAUTREBANDE.

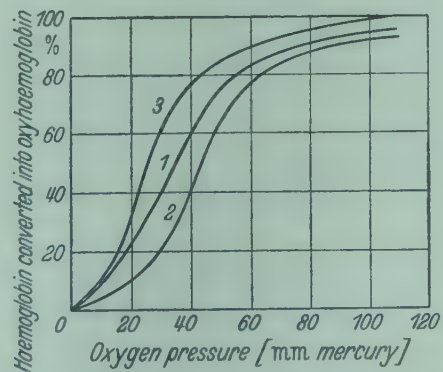


Figure 7. Dissociation curves for oxyhaemoglobin at different pH values of the blood, curve 1 for normal pH, curve 2 for low pH (acidosis), curve 3 for high pH (alkalosis); after DAUTREBANDE.

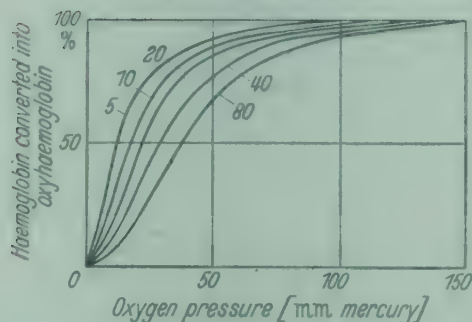


Figure 8. Dissociation curves for oxyhaemoglobin in equilibrium with carbon dioxide at 5 to 80 mm Hg pressure, figures on the curves indicating equilibrium carbon dioxide pressures in the range (DAUTREBANDE).

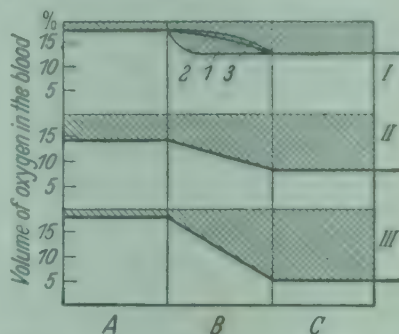


Figure 9. Oxygen content of the blood. The hatched areas represent haemoglobin, the blank areas oxyhaemoglobin (DAUTREBANDE). A arteries, B capillary vessels, C veins; I normal, II oxygen deficiency in arterial blood, III same in capillary vessels and veins caused by insufficient circulation. II and III are cases of cyanosis.

In order to ensure that the complete removal of the carbon dioxide produced in the tissues automatically corresponds to the oxygen demand, the carbon dioxide-bicarbonate equilibrium is adapted to the oxygen pressure of the atmosphere. Normally the pH of the blood is 7.35 and the ratio  $\text{CO}_2:\text{HCO}_3$  is 1:20 (Figure 10).

At high altitudes the oxygen pressure of the air is low and we have to breathe more frequently and deeply to satisfy our oxygen requirement. If the bicarbonate concentration should remain the same the enlarged ventilation of the lungs would eliminate too much carbon dioxide, so the bicarbonate content of the blood has to be readjusted at a lower level, the  $\text{CO}_2:\text{HCO}_3$  ratio (and thereby the pH of the blood) having to remain constant. Extra adaptation to a constant low oxygen pressure is realized by an increase in the number of red corpuscles, Figure 11.

Of the mutually proportional factors, energy, oxygen consumption and carbon dioxide production, the carbon dioxide formation provides for the automatic instantaneous adjustment of the respiratory volume, while the bicarbonate content of the blood adjusts the level at which the exchange of carbon dioxide takes place, adapting it to the available oxygen pressure.

In addition to these factors and coordinated with them there exists a close relationship between respiration and blood circulation which functionally must be considered as one system. It is known, for instance, that the number of capillaries through which the blood flows, and also their width, are directly influenced by the final products of the respiratory metabolic process. The heart centre is also influenced by these final products, and will be stimulated or retarded according to the needs.



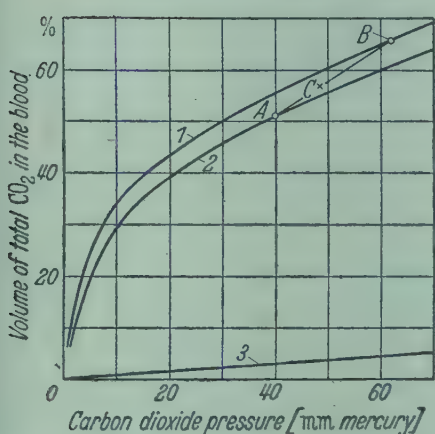


Figure 10. 1 dissociation curve for  $\text{CO}_2$  in completely reduced blood, 2 saturation curve for  $\text{CO}_2$  in completely oxidized blood, A arterial, B completely reduced and C normal venous blood, 3 percentage of free  $\text{CO}_2$  in blood. (At the normal  $\text{CO}_2$  pressure in the alveoli (40 mm Hg) the blood contains 51 volumes per cent of total  $\text{CO}_2$  (after DAUTREBANDE).

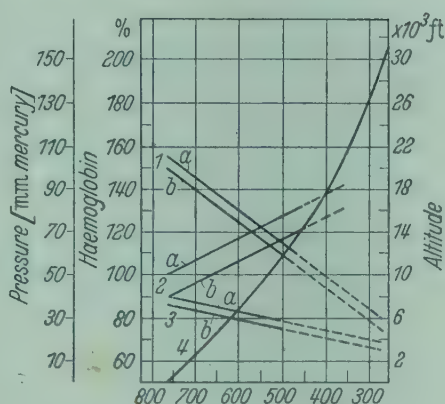


Figure 11. Adaptation of oxyhaemoglobin content of the blood to the available oxygen pressure (altitude) for *a* men *b* women: 1 oxygen pressure in the alveoli, 2 haemoglobin content of the blood, 3 carbon dioxide pressure in the alveoli, 4 barometric pressure (DAUTREBANDE).

If the body requires more oxygen the respiration becomes deeper, the lungs expand, and parallel to these phenomena the blood pressure is raised so that the surface of the capillaries through which the blood flows is enlarged. Under normal conditions all regulating factors cooperate ideally, not only to provide for the necessary oxygen supply and complete removal of the carbon dioxide produced but also for an efficient distribution and transport through the body.

**Regulation of blood composition**—For the normal functioning of the body it is essential that the composition of the blood and especially its pH should remain constant within narrow limits. This is attained:

- a* as a result of the amphoteric character of the albumens in the blood plasma which act as a buffer
- b* through the buffering action of the carbon dioxide-bicarbonate equilibrium, which is made possible by the alkali reserve of the blood
- c* because the kidneys can produce and eliminate acids according to the requirements
- d* by the removal of carbon dioxide in the lungs.

Some of these adaptations are spontaneous (*b* and *d*); others such as *c*, and also the bicarbonate level, are adjusted gradually.

**Oxygen deficiency**—Circumstances sometimes arise in which the oxygen supply of the tissues becomes insufficient. Obviously such conditions will have serious consequences. Oxygen deficiency may be the result of four different causes :

- 1 the saturation of the haemoglobin with oxygen may be insufficient
- 2 the quantity of haemoglobin may be insufficient
- 3 the blood circulation itself may be too slow to supply the tissues with a sufficient quantity of oxygen within a given time
- 4 the tissues may not be able to use the oxygen supplied by the haemoglobin.

Insufficient saturation of the haemoglobin is caused by :

- i insufficient ventilation of the alveoli (asthma, shallow breathing, oedema of the lungs, pneumonia)
- ii increased breathing resistance *e.g.* in using a respirator with a high resistance
- iii low oxygen pressure of the available air *e.g.* at high altitudes (in aircraft or in climbing high mountains) or in mines with insufficient ventilation.

Insufficient quantity of available haemoglobin is typical in carbon monoxide poisoning. Here the haemoglobin is blocked by the carbon monoxide. Shortage of haemoglobin is also a symptom of anaemia.

Loss of large quantities of blood in accidents or after operations and haemolysis by blood-destroying poisons also results in haemoglobin shortage.

Insufficient circulation is present in heart failure or in dilation of the vessels by shock, collapse or diseases of the circulatory system.

Cyanide ions and hydrogen sulphide interfere with the metabolism of the tissue cells by a paralysing action on the respiratory ferments. Oxygen is supplied in abundance but the cell substance is not able to use it for its metabolic processes.

When oxygen deficiency occurs the organism tries to make up for it by accelerated respiration. As a result of this too much carbon dioxide is removed from the blood. The consequence is that the respiration stops as soon as the carbon dioxide content falls lower than the threshold value below which the respiratory centre is no longer excited. Prolonged artificial respiration may also cause the carbon dioxide content of the blood to drop below the critical value.

When the oxygen pressure of the available air falls below a given value (about 100 mm Hg) the consequence may be serious, especially as the fatal stage is reached suddenly without the victim noticing it.



**Physiological effects of atmospheric poisoning**—When the air contains a substance which is detrimental to health this substance may damage the outer respiratory tract, be absorbed in the lungs and transported by the blood. Some substances irritate the air passages and thereby cause acute disturbances of the respiration (coughing, suffocation by chlorine) as well as inflammation of the mucous membranes, while the absorption and transportation of the toxic substance by the blood results in a rapid and efficient distribution of the poison through the body.

Some substances interfere with the metabolism of the cells. The nervous system is particularly susceptible. It reacts both to a shortage of oxygen and to the presence of most toxic substances. As a rule nervous disturbances are observed before physical symptoms appear.

**Physiological data**—Some data concerning basic metabolic rates of blood and urine are tabulated in Table 6.

Table 6. Physiological data for the Human Organism

<i>Basic metabolic rate</i> ... ..	—10 per cent to + 10 per cent 40 cal per m <sup>2</sup> per hr 1,800 cal per 24 hr
<i>Blood :</i>	
<i>Oxygen capacity</i> ... ..	18 to 24 per cent by volume
<i>Oxygen content, arterial blood</i> ...	15 to 23 per cent by volume
<i>venous blood</i> ...	10 to 18 per cent by volume
<i>pH arterial</i> ... ..	7.3 to 7.35
<i>venous</i> ... ..	7.2 to 7.25
<i>Water content</i> ... ..	77 to 81 per cent by weight
<i>Red blood cells</i> ... ..	4.2 to 5.5 million per mm <sup>3</sup>
<i>White blood cells</i> ... ..	5 to 10 thousand per mm <sup>3</sup>
<i>Platelets</i> ... ..	200 to 500 thousand per mm <sup>3</sup>
<i>Average diameter of red blood cell</i> ...	7.5 $\mu$
<i>Haemoglobin, adults females</i> ...	12.8 to 15.2 gm per 100 ml
<i>males</i> ...	14 to 17 gm per 100 ml
<i>Sedimentation rate, Westergren</i> ...	less than 20 mm per hr
<i>Blood volume, per kg bodyweight</i> ..	70 to 100 ml
<i>per m<sup>2</sup> body surface</i> ..	2,800 to 3,800 ml
<i>Venous pressure, peripheral vein</i> ..	60 to 100 mm water column
<i>Vital capacity</i> ... ..	3,500 to 4,500 ml
<i>Urine :</i>	
<i>Chlorides as NaCl</i> ... ..	10 to 15 gm per 24 hr
<i>Glucose</i> ... ..	0.5 to 1 gm per 24 hr
<i>Phosphates as P<sub>2</sub>O<sub>5</sub></i> ... ..	2 gm per 24 hr
<i>Sulphates as SO<sub>3</sub></i> ... ..	1.8 to 3.0 gm per 24 hr

## CHEMICALS AS POTENTIAL POISONS

In a chemical laboratory chemicals are tools, and we become so familiar with them that we are apt to forget that a great many are detrimental to health when they get into the system. Several substances have a bad reputation *e.g.* arsenic and potassium cyanide, but there are a great many substances which are as dangerous without our realizing it.

The insidious slow-working poisons are the most hazardous. Every chemist should acquire an adequate knowledge of the physiological action of the chemicals he deals with, and learn always to handle them with care.

Our knowledge of the physiological action of chemicals has lagged behind in comparison with the development of science in general. Conditions in the laboratory or the chemical factory can menace health in a way not yet fully recognized. There are many examples of research workers suffering by being unaware of the toxicity of the material or radiations with which they work, as shown by the following examples from chemical history<sup>2</sup>.

GAY LUSSAC had several accidents through explosions. He suffered much from them and they finally caused his death. The discovery of nitrogen trichloride cost DULONG an eye and three fingers. BUNSEN lost an eye as the result of an explosion and suffered from chronic mercury poisoning. BECKMANN was poisoned by diazomethane which he discovered. Several investigators have fallen victim to the action of x-rays and radioactive substances.

Neatness and cleanliness are essential in the laboratory for more than one reason. Some chemicals have an instantaneous detrimental effect on the living tissues with which they come in contact *e.g.* very reactive and strongly dehydrating reagents. Well known examples are concentrated acids and alkalis, and anhydrous aluminium chloride. They react especially in the presence of moisture and for that reason have a most serious effect on the eyes and mucous membranes. Other chemicals act as real poisons interfering with cell metabolism, or by their action on the blood. Many chemicals have a detrimental effect on the respiratory system.

**Defence mechanisms**—The action of toxic chemicals is primarily determined by the concentration attained in the body fluid. When a relatively small quantity of a foreign substance gets into the body our organism may react in a variety of ways, for instance :

- a* by alterations in the blood circulation (expansion of the blood vessels, lowered blood pressure, increased number of blood corpuscles, change of the *pH* of the blood) and the physiological function of the organs (stimulated action of the

excretory organs, accelerated respiration, vomiting, diarrhoea, changes in the metabolic process of the cells)

- b* by alterations of the toxic substance foreign to the organism, rendering it less harmful (by oxidation, reduction, hydrolysis, synthesis, decomposition, deposition or elimination)
- c* by adaptation in trying to establish a new equilibrium under the modified circumstances.

This natural defence is influenced by the general condition of health. If, however, the concentration of foreign substance passes a threshold value the natural defence of the body cannot cope with it. The result is functional disorder of one or more organs, sometimes combined with or followed by anatomic alterations which may be permanent. Living tissues may be destroyed or abnormal cell growth stimulated.

**Cumulative effects**—If the foreign substance is not excreted, or insufficiently so, small quantities of the substance, by themselves too small to do much harm, accumulate in the body. By repeated absorption of minute quantities of a foreign substance the definitely toxic amount will finally be exceeded. Such accumulation is well known with lead and mercury compounds.

Accumulation may also give rise to gradually aggravating symptoms such as a change of the blood and tissues. Repeated absorption in the body of certain substances often brings about an increased sensibility.

In other instances the sensitivity decreases (*e.g.* arsenic). Sometimes a person shows symptoms of supersensitivity to minute quantities of certain substances. As a result of this, substances which would not normally harm the organism give typical and often serious reactions in some individuals (allergy). This may result from repeated contact with the substance. Bronchial asthma, inflammation of the mucous membranes of eyes, nose and throat, oedema, reactions of the stomach and intestines, and eczema, are examples of such allergic reactions. The general condition of the organism has an important influence on the predisposition to such ailments.

**Immediate effects**—As regards their immediate effects we may distinguish between substances which, when they enter the body, cause irritations, thereby betraying their presence by smell, taste, irritation of the mucous membranes, lachrymation or sternutative action, painful, stinging, itching sensations: and substances which do not betray themselves because the body does not give adequate warning, since their reaction is not unpleasant or the body soon becomes accustomed to it. This applies to a great many gaseous poisons such as carbon monoxide, amyl acetate, benzene and



phosgene as well as to mercury and lead compounds and also to x-rays and radioactive rays<sup>3, 4</sup>.

As a rule the substances of this latter group are the most dangerous. When a substance betrays itself by its irritating reaction it is automatically handled carefully or avoided.

Substances which have no appreciable action on the senses or which do not cause the organism to offer resistance by reflex reactions are very dangerous. They require acquaintance with their properties and a good training in manipulation and technique. The same is true for substances with a cumulative effect. The disturbances are apt to develop gradually until they have become permanent and it has become too late to take any effective measures.

The first symptoms of a poisoning are seldom specific or obviously related to the chemical or physical properties of the toxic substance, because they are the result of disturbances in the metabolism of the cells, which may also be the consequence of a disease, malnutrition, and over-fatigue. Moreover they are subjective (fatigue, headache, dizziness, indigestion).

Poisonings are often classified as acute and chronic cases. This distinction may refer to the duration of the process ; other authors call a poisoning acute when it is the result of one single absorption of the toxic substance and chronic when it is the result of repeated absorptions of small quantities.

## MODE OF ENTRY AND ACTION OF TOXIC SUBSTANCES

**Entry via the lungs**—Gases, dust, mist, aerosols *etc* may enter the respiratory system. The substances may irritate the mucous membranes of the throat and trachea, and subsequently cause secondary infections. In the lungs the substance can be absorbed in the blood. The velocity with which a gas is absorbed in the blood is determined by its partial pressure and the frequency and depth of respiration.

**Entry via the stomach**—This mode of entry<sup>5</sup> is usually the result of uncleanness or carelessness whereby toxic substances may enter the body and be absorbed in the intestines. Eating and drinking in the laboratory is therefore undesirable and should be prohibited. The rule will be obeyed the more readily if a clean room is provided where snacks may be consumed. The danger is illustrated by an accident which might have been fatal.

A laboratory worker had made some tea for his lunch and meanwhile continued with his work. By mistake he put two spoonfuls of phenol instead of sugar in his tea (the bottles of sugar and phenol were side by side on the bench). He stirred and took a good draught. Fortunately he did not swallow.

The hands ought, normally, to be washed with warm water and soap. It is often advisable when washing after having one's hands stained with chemicals to wash with cold water first. If the chemical is one which is easily absorbed through the skin the hot water will tend to open the pores and facilitate its entry. Preliminary removal of the greater part of the chemical with cold water will lessen this risk. This procedure should always be adopted for removing a bad splash.

In England most regulations for dangerous trades include a statutory requirement that washing facilities including towels, soap and hot water must be provided for the use of all persons concerned.

To revert again to smoking : it is unwise to smoke cigarettes when the hands are dirty with chemicals in case the chemical permeates the cigarette paper, is vaporized and drawn into the mouth.

Handling a pipette frequently causes accidents, especially with iodine or alkali hydroxide solutions. A safety pipette or a pump should be used.

**Entry via the skin**—The undamaged skin is impermeable for many substances but small wounds provide a point of entry. Among the chemicals which irritate or damage the skin are :

*a* fat solvents (benzene)

*b* tissue destroying substances (dehydrating agents, oxidants)

*c* protoplasmic poisons (hydrogen fluorides, phenol).

The skin has a very important task in maintaining the body in a healthy condition. It helps to regulate the body temperature, protects against germs and it is one of the secretion organs. As soon as the skin is damaged it becomes more permeable to germs and cannot function properly.

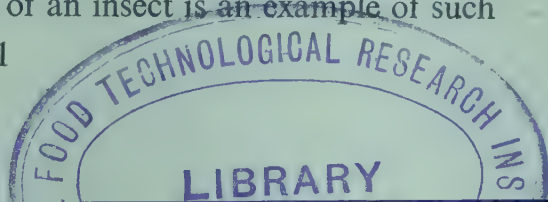
Chemicals may cause an irritation (itching) followed by inflammation (redness), moisture secretion (blisters ; danger of a secondary infection when blister bursts), scaling of the epidermis (photographic developers, phenols), formation of scars, necrosis and cancer.

The effect of chemicals on the skin resembles that of high or low temperature: chemical burns. Sometimes discoloration occurs, while by continued action certain substances cause a persistent eczema (fat solvents, nitro compounds).

Subjective sensitivities are often very different. It is advisable to make frequent use of rubber gloves and fingers.

Some chemicals have a specific action. A typical example is the action of chlorobutadiene. In factories where this substance is polymerized the operators are reported<sup>6</sup> to suffer from loss of hair.

**Entry by injection**—Toxic substances may reach the body liquids by hypodermic injection. The sting of an insect is an example of such





a possibility. Aniline poisoning has been described which was caused by the breaking and sticking into the wound of the sharp point of an indelible pencil.

**Action on the eyes**—The external membrane of the eyeball and the cornea are extremely sensitive to chemicals. Naturally the consequences here are much more serious than on the skin, hence safety goggles should be used frequently, especially when pulverizing or sieving substances. When some irritating substance has entered the eye the best thing to do is to flush immediately with an abundance of water and take the advice of the oculist as soon as possible.

**Active concentration**—Some substances even in minute quantities have a strongly irritating effect on the body. We need only refer to the lachrymatory and sternutatory substances which were applied in the 1914-18 war. Such substances have to be handled frequently in the organic laboratory. Tables 33 and 34 (pp 209, 210) give an idea of sensitivity to such substances.

**Fatal dose**—With solid or liquid poisons the fatal dose  $W$  is determined by the formula

$$W = g/G \quad \dots \dots (1)$$

where  $g$  is the dose of the poison, gm,  $G$  the weight of the body in kg. The quotient  $g/G$  is practically constant for most warm blooded animals and man, and is specific for the poison. With gases  $g$  is difficult to determine. Here the amount of poison inhaled is

$$g = ct.A \quad \dots \dots (2)$$

where  $c$  is the concentration of the gas, mg/m<sup>3</sup>,  $t$  the time of exposure, min, and  $A$  the litres of air inhaled per minute.

Substituting equation 2 in equation 1 gives for gases the formula

$$W = ct.A/G \quad \dots \dots (3)$$

For a person at rest,  $A = 10$ , and for a person hard at work,  $A = 100$ . For substances with a cumulative effect the  $ct$  values have to be added, so that the fatal dose can be reached by a succession of non-fatal doses.

After the substance has been absorbed it is transported through the body by the blood and distributed over the tissues and the organs. Some poisons affect all organs ; others have a specific local action on definite organs. The nervous system is very sensitive to the action of many foreign substances.

The substance may then be converted into compounds which on account of their solubility are more easily eliminated with the urine or, owing to their insolubility, are apt to be deposited ; for instance, lead is deposited as phosphate in the bones. Sometimes the reaction products are much more toxic than the original substance. All



such reactions take place by the catalytic action of enzymes : the study of these reactions has helped in finding antidotes for specific poisons.

The metabolic rate of foreign substances, the so-called detoxication mechanism, has been the subject of extensive study. The term detoxication includes not only changes involving a reduction in toxicity but also those involving an increase in toxicity. The more usual detoxication reactions are oxidative, reductive or synthetic in nature.

Primary alcohols are oxidized to acids, aromatic hydrocarbons to phenols. Aromatic nitro compounds are reduced to amines, ketones to alcohols. Several substances are transformed to glucuronides, phenols to an ethereal sulphate. Many aromatic compounds are subject to the glycine conjugation, others to the glutamine synthesis. Hydrogen cyanide can be detoxicated<sup>7</sup> by the conversion of the cyanide to the non-toxic thiocyanate radicle.

The toxic substance or its reaction products can be eliminated by the lungs, by the skin, *via* the intestines, or by the kidneys or the liver. The respective organ may consequently be damaged.

Many toxic substances influence each other's toxicity. For instance, the effect of many poisons is more serious after the consumption of alcohol. It was found that carbon monoxide and benzene together have a marked cumulative toxic effect. A rise in temperature considerably increases the toxic effect of benzene<sup>8</sup>. Other substances counteract each other as with an antidote. The toxicity of most substances is usually based on their disturbing the metabolism of the cells or on their action on vitamins or hormones.

**Toxic gases, vapours, mists and fumes**—Some inert gases can be noxious only when as the result of their presence the oxygen concentration of the atmosphere is lowered appreciably (nitrogen, carbon dioxide). Many others have a specific toxic action, some when they are present in low concentrations. The action of others is restricted to an affection of the mucous membranes of the throat, trachea, bronchi and lungs. Even when such substances are not absorbed in the blood and do not react with the constituents of the blood or the internal organs and tissues, they impede the respiration, thus causing oxygen deficiency or even death by suffocation.

The vapour pressure and especially the solubility in water influence the depth to which such a toxic gas penetrates the air passages. With highly water-soluble compounds (ammonia, volatile strong acids) the affection is restricted to the upper air passages : throat, trachea, bronchi.

Less soluble gases also penetrate into the lung (sulphur dioxide, hydrogen sulphide, chlorine). There are some gases that, while

having practically no irritating action on the upper respiratory tract, easily find their way into the lungs, where they exercise their detrimental effect (nitrogen dioxide, phosgene).

The affection of the mucous membranes is started by an expansion of the blood vessels (redness) and secretion of lymph. If it proceeds the blood vessels start to secrete plasma, which tends to solidify and be eliminated. The results are swelling, narrowing and obstruction of the pharynx and bronchi.

The affected mucous membranes are moreover liable to infection, so that the affection is mostly followed by an infectious process. If the lungs are affected the blood plasma fills the alveoli, causing lung oedema. The active volume of the lungs thereby diminishes, causing oxygen deficiency and finally suffocation (nitrogen oxides, phosgene).

**Narcotics**—A great many organic compounds (hydrocarbons, alcohols, esters, chlorinated aliphatic hydrocarbons) which are absorbed in the blood from the lungs and subsequently distributed through the body have a specific effect on the nervous system, as a result of their fat dissolving capacity. In the initial stage the effects are dizziness, headache, drowsiness and sometimes hilarity resembling intoxication by alcohol. This initial stage is followed by a stage of excitation (delirium) after which the patient becomes unconscious and the reflexes disappear. In still higher concentrations the narcotic damages the respiratory centre, thus causing death (Table 37, p 212).

Generally with a homologous series of hydrocarbons or alcohols the narcotic action increases with the molecular weight. If the number of alcohol groups increases the narcotic action diminishes. The carboxyl group eliminates the narcotic action but with the formation of esters it is more or less restored. With the aliphatic hydrocarbons the narcotic action is greatly increased if hydrogen is substituted by chlorine. Moreover the chlorinated hydrocarbons exercise a specific toxic action on various organs (liver, kidneys and heart). With the aldehydes the irritation of the mucous membranes becomes more prominent. With aromatic hydrocarbons (benzene), amines (aniline) and nitro compounds the detrimental effect on the blood is the most important.

**Blood poisons**—Several substances by causing changes in the blood act as blood poisons. The change may involve both the blood corpuscles and the plasma. We may distinguish between :

*a* substances which act on the red blood cells

*b* substances which upset the equilibrium in the blood because



they modify the concentration and composition or the acidity of the solution

- c substances which influence the production of red blood cells and of white cells.

Numerous poisons cause disintegration of the red blood corpuscles (haemolysis) followed by excretion of haemoglobin in the urine (haemoglobinuria). Others oxidize the haemoglobin to the stable methaemoglobin<sup>9</sup>.

With the aromatic amines and with nitroso and nitro compounds the toxic action is primarily due to this conversion of the haemoglobin into methaemoglobin, which compound is so stable that it cannot give up its oxygen to the tissues, thus causing oxygen deficiency. Moreover the formation of methaemoglobin is followed by destruction of the red blood corpuscles. The methaemoglobin passes into the blood, after which it is secreted in the urine. Part of it is transformed into bile and causes jaundice.

Nitrites and substances containing the R-N-NO group cause a dilation of the arteries, so that the blood pressure falls and the blood circulation is upset, causing a considerable decrease in the oxygen supply to the organs, thereby affecting the nervous system and the respiration.

**Substances affecting the skin**—All kinds of irritating, corrosive and fat dissolving substances, as well as aromatic nitro and amino compounds, may cause skin diseases. Frequently an individual hypersensitivity manifests itself.

The skin is defended by the horny layer composed of keratin which is insoluble in water, alcohol and acids, and by the secretions of the sebaceous glands ; sweat, which dilutes the irritating substance, and cholesterol and waxes, which give protection against water soluble substances.

The horny layer is softened by alkalis, and fat solvents may penetrate into the pores of the skin. Heavy metal ions precipitate the skin proteins. Some chemicals have a desiccating action.

Fluorides paralyse the cell metabolism. Some substances stimulate the horny layer and at times lead to new growths. The most common skin irritants are :

- a organic solvents : petroleum spirit, turpentine, petroleum, benzene, toluene, xylene and many other organic substances such as gas oil, creosote, tar, carbolineum and pitch. Phenols and aromatic amino and nitro compounds are particularly liable to cause eczema *e.g.* photographic developers, trinitro-toluene (trotyl), tetryl, trinitrophenol, methylnitramine, aniline dyes and dinitrochlorobenzene.

- b* alkalis : ammonia, lime, cement, alkali cyanides, hydroxides and carbonates, trisodiumphosphate, water glass and alkali sulphides.
- c* strong acids, especially hydrofluoric acid, as well as many salts such as soluble fluorides, zinc chloride and potassium nitrate, fertilizers *e.g.* calcium cyanamide, and oxidizing agents such as persulphates and bleaching powder.
- d* chromic acid and chromates which are specific skin poisons.

### PROTECTIVE MEASURES

**The skin**—Ideal protection of the skin is achieved by preventing contact with the irritant substance *e.g.* by handling in closed apparatus. When this is impossible special clothing such as rubber gloves, impervious sleeves and aprons, masks and goggles should be used. It is essential that any apron used should come over the top of rubber boots worn ; otherwise it is likely that material splashing on to the apron will run down inside the boots.

Protective clothing should be inspected, repaired and cleaned daily. When working with irritant substances a shower bath should be taken after work. Where there are special skin hazards a double set of locker rooms should be provided, one for street and one for working clothing. After work the soiled working clothes are removed in the room with the locker for soiled clothing ; then after a bath street clothes are put on in the second locker room. Even the slightest irritation of the skin should be reported to the Medical Officer at once. There should be periodical medical examinations.

During the 1939-45 war the protection of the skin by protective ointments was extensively developed. For this purpose several barrier creams have been introduced under the name of 'invisible gloves'. They are still in a state of development and experiment and should be so considered. There is a chance that their development will prove satisfactory in many circumstances. If, however, the noxious agent against which protection is sought is soluble in the barrier cream, the barrier becomes a carrier, and gives an increased toxic effect instead of protection.

At the moment it is advisable to use barrier creams only where the relationship between the toxic substance and the constituents of the cream is well known. Barrier creams of unknown composition should not be used. For every group of agents the protective cream should comply with a definite set of specifications.

Even when such different creams have been developed, circumstances will always remain when it is necessary to rely on gloves made of a material impermeable to the irritant substance.



## PROTECTIVE MEASURES

**The eyes**—Eye irritations, such as swelling of the eyelids, inflammation and damage to the cornea and conjunctiva, are caused by corrosive substances such as acids, alkalis, many salts, hydrogen sulphide and a great many organic compounds.

Protection by suitable goggles, preferably of the monogoggle type made of plastic, is necessary. Medical aid should be sought for any injury of the eyes.

**Protection against ultraviolet and infra-red rays**—The action of ultraviolet rays is acute, causing inflammation of the conjunctiva. Infra-red rays may cause haziness of the cornea and produce cataract of the lens.

Excessive brightness of visible rays may cause eye strain and irritation. For this reason the glasses used in welding have to be of a dark shade impermeable to ultraviolet light. On the other hand the worker must have clear and accurate vision. Protective glasses should therefore be selected and tested with care (Table 48, p 232).

Ultraviolet rays are absorbed in the outer layers of the eye, the cornea and conjunctiva. The result is conjunctivitis, beginning four to eight hours after the exposure and lasting for several days. In order to avoid secondary infection the eye should not be rubbed by the patient. A sterile dressing is advisable.

Protective glasses have been analysed by the U.S. National Bureau of Standards, and a table gives the properties of each 'shade' of glass (Table 49, p 233). Each man should have his own goggles. Goggles should not be exchanged, to prevent contamination. Sterilizing of protective equipment at intervals is advisable.

The Council on Physical Therapy of the American Medical Association has suggested that individuals should not be exposed to intensities of ultraviolet rays exceeding  $0.5$  microwatt per  $\text{cm}^2$  during a seven hour period, and not more than  $0.1$  microwatt per  $\text{cm}^2$  for a continuous 24 hour day.

All workers should take especial care of the eyes, protecting them if necessary with goggles of good mechanical and optical qualities.

**Radiation hazards**—Increased knowledge has greatly reduced the number of injuries from radiation during and since the 1939-45 war. The hazard in industry comes from ingestion, external radiation, and inhalation of radioactive dust and radioactive disintegration products.

In laboratories where radioactive isotopes are used as tracers or otherwise there should be a trained health physicist on the staff.

Shielding with lead of the necessary thickness, controlled equipment and adequate ventilation can be useful in giving protection from radiation and absorption of radioactive material. The Geiger-

Müller counter is a means of detection of the most noxious gamma radiation. Repeated control of personnel and equipment is necessary at short intervals. Periodic medical examination, including blood counts, may lead to preventive measures. All personnel should be instructed in avoiding the hazards that threaten them.

## TOXICITY AND CHEMICAL CONSTITUTION

Generally speaking, investigations into the toxicity of chemical compounds have to be made on animal subjects, and it is usual to select an animal which it is hoped will give a reaction most nearly approaching that of a human being. This decision can only be taken after a preliminary scheme has shown which organ is particularly susceptible to the poison concerned. It has so far proved almost impossible to foresee with any precision the toxic effects on man of a given concentration of a vapour by deduction from the results of animal experiments, and therefore an approximation has usually to be made. This naturally is given a very large safety factor.

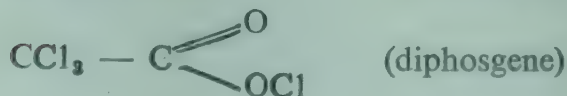
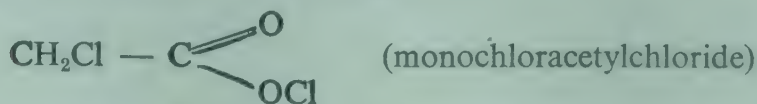
The study of the relation between toxicity and chemical constitution of a substance is still in its initial stage. In the series of the aliphatic hydrocarbons and alcohols the toxicity increases with the number of carbon atoms. Increase of the number of hydroxyl groups decreases the toxicity. Introduction of halogen gives an organic substance aggressive properties.

Table 7. Effect of halogen on lachrymatory properties

<i>Substance</i>		<i>Formula</i>	<i>Max tolerable concentration mg/m<sup>3</sup> air</i>
<i>Chloracetone</i>	... ..	$\text{CH}_3\text{CO}\cdot\text{CH}_2\text{Cl}$	18
<i>Bromacetone</i>	... ..	$\text{CH}_3\text{CO}\cdot\text{CH}_2\text{Br}$	1
<i>Benzyl bromide</i>	... ..	$\text{C}_6\text{H}_5\cdot\text{CH}_2\text{Br}$	4
<i>Benzyl iodide</i>	... ..	$\text{C}_6\text{H}_5\cdot\text{CH}_2\text{I}$	2

**Halogens**—Some compounds containing halogen atoms have lachrymatory properties, Table 7.

With more halogen atoms the irritating action decreases and the toxicity increases, as for instance :





In the 2-position the halogen atom will cause stronger irritation than in the 1-position. With aromatic compounds the halogen atom has a tear-exciting effect in the side chain, but in the ring it is inactive. Compare, for instance, benzyl bromide  $C_6H_5CH_2Br$  and bromotoluene  $(C_6H_4Br)CH_3$ .

**Sulphur**—Sulphur promotes the capacity of a substance to penetrate into the skin, as exemplified by  $O(CH_2.CH_2Cl)_2$  and by  $S(CH_2.CH_2Cl)_2$ , whereas the toxicity of sulphur compounds decreases with increasing valence of the sulphur in the series :



**Arsenic**—Trivalent arsenic is poisonous, particularly when it is linked to two identical atoms or atom groups and another atom (atom group) such as in  $C_6H_5AsCl_2$  and  $(C_6H_5)_2AsCl$ .

In combination with unsaturated groups arsenic is a vesicant ; combined with aromatic groups it has a strongly irritating action.

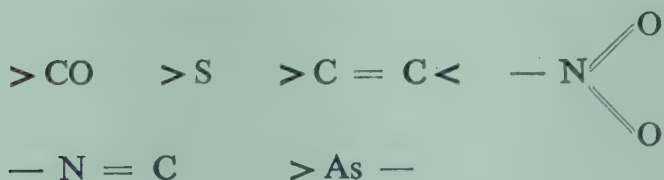
**Nitro groups**—The nitro group intensifies the lachrymatory properties of a substance *e.g.* *o*-nitrobenzylchloride.

The toxicity of nitro compounds increases with the number of nitro groups. The substitution of chlorine in nitro compounds increases the toxicity. The toxicity of chloronaphthalenes increases considerably with the number of halogen atoms in the molecule.

The double bond increases the toxicity as opposed to the irritating action of a substance ; compare for instance propionaldehyde  $CH_3.CH_2.CHO$  and acrolein  $CH_2=CH.CHO$ .

**Classification of toxicants**—Some authors classify organic substances according to their toxic action, using classification analogous to that of dyes (EHRlich, NEKRASSOV, JANKOVSKY).

The toxophore group gives the substance a potential toxicity *e.g.*



The autotoxic group transforms the latent into active toxicity *e.g.* Cl, O,  $-NH_2$ , benzyl, phenyl, methyl, ethyl. Some examples are given in Table 8.

**Carcinogenic substances**—Several aromatic compounds have carcinogenic properties. Coal tar for instance contains a slight amount of 3,4-benzpyrene, the originator of the tar or pitch cancer of the skin. Aromatic hydrocarbons with carcinogenic properties can be

Table 8. Classification of Toxic Groups

<i>Toxophore group</i>	<i>Autotoxic group</i>	<i>Examples</i>	<i>Formula</i>
<i>Halogen</i>	<i>methyl phenyl benzyl</i>	<i>dichlormethylether benzylbromide</i>	$\text{ClCH}_2.\text{O}.\text{CH}_2\text{Cl}$ $\text{C}_6\text{H}_5.\text{CH}_2\text{Br}$
$> \text{CO}$	<i>halogen double bonds</i>	<i>acetone bromide chloracetophenon phosgene acrolein</i>	$\text{CH}_3.\text{CO}.\text{CH}_2\text{Br}$ $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_2\text{Cl}$ $\text{COCl}_2$ $\text{CH}_2:\text{CH}.\text{CHO}$
$> \text{S}$ $> \text{SO}$ $-\text{SO}_2$	<i>halogen methyl</i>	<i>dichlorethylsulphide dialkyl sulphonates</i>	$\text{S}(\text{CH}_2.\text{CH}_2\text{Cl})_2$ $\text{O}:\text{S}(\text{OR})_2:\text{O}$
$-\text{C}:\text{N}$ $-\text{N}:\text{C}$ $-\text{NO}_2$	<i>halogen benzyl</i>	<i>hydrogen cyanide bromobenzylcyanide picric chloride</i>	$\text{HCN}$ $\text{C}_6\text{H}_5.\text{CH}(\text{CN})\text{Br}$ $\text{CCl}_3.\text{NO}_2$
$\text{As}\equiv$	<i>alkyl phenyl</i>	<i>diphenylchlor arsine phenarsazin chloride</i>	$(\text{C}_6\text{H}_5)_2.\text{AsCl}$ $\text{NH}(\text{C}_6\text{H}_4)_2\text{AsCl}$

derived from the harmless 1,2-benzanthracene. By substitution carcinogenic compounds are formed as are shown on p 61.

Such substances exercise their detrimental influence even when present in very slight amounts, in this respect resembling the action of vitamins and hormones.

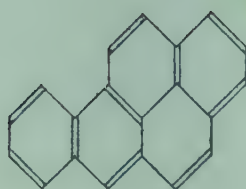
The aromatic amines and azocompounds are another group of carcinogenic substances, causing especially liver and bladder tumours. For example 2-naphthylamine, benzidine, azotoluene, *o*-amidoazotoluene, *p*-dimethylamidoazobenzene. Such substances, even when absorbed in minute quantities, may cause bladder tumours after many years.

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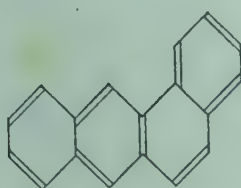
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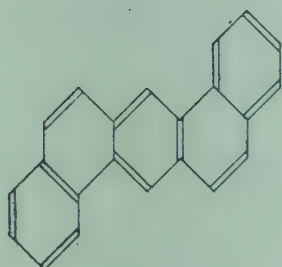
# TOXICITY AND CHEMICAL CONSTITUTION



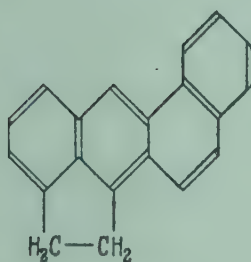
3, 4-benzpyrene



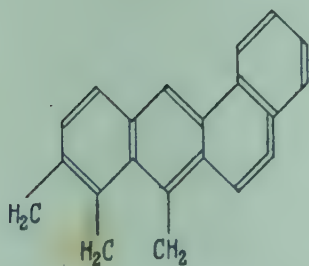
1, 2-benzanthracene



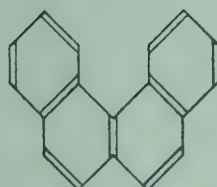
1, 2, 5, 6-dibenzanthracene



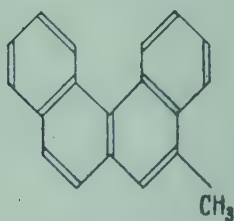
cholanthrene



methylcholanthrene



3, 4-benzphenanthrene



2-methyl-3, 4-benzphenanthrene

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## HANDLING TOXIC AND INJURIOUS SUBSTANCES IN THE LABORATORY

### ACIDS

**Sulphuric**—Concentrated sulphuric acid and oleum cause burns on the skin and have a destructive action on all tissues. They destroy the clothes and are fatal to the eye. When diluting sulphuric acid the strong acid should be poured carefully into the water ; water should never be poured on to the strong acid.

Fumes and droplets produce severe irritation of the respiratory tract. Inhalation of the vapour of hot acid may cause loss of consciousness with serious damage to the lung tissue. Workers exposed to low concentrations lose their sensitivity to the irritant action. Sulphuric acid burns are deep and produce scars.

**Hydrochloric**—Gaseous hydrochloric acid is a primary irritant with a destructive action on mucous membranes, causing necrosis, pulmonary oedema, and inflammation and ulceration of the upper respiratory tract and of the conjunctiva.

**Nitric**—Concentrated nitric acid etches the skin : the yellow stain due to reaction with albumens disappears only after a considerable time. Continued action causes an open wound, sometimes neuritis. Nitric acid vapour is a serious respiratory poison. Nitric acid is also a powerful oxidant, causing fire hazards when mixed with combustible materials. Traces of an organic substance with nitric acid and mercury may form a highly explosive fulminate. Mixtures of nitric and sulphuric acid may be very dangerous and can only be safely handled when the user is fully aware of the hazards involved.

**Hydrofluoric**—Hydrofluoric acid has an etching action on the skin and even at low concentration (1.5 mg HF per litre of air) affects the mucous membranes of the respiratory organs. Prolonged inhalation of 15 mg of hydrofluoric acid per cubic metre of air causes chronic affection of the respiratory tract, of the eyelids and especially of the eyes. Eventually total blindness may result. This is an occupational disease with persons whose daily work consists in etching glass with hydrofluoric acid.

The concentrated acid produces open wounds. With diluted acid the irritation of the skin and of the tissues becomes noticeable only

## GENERAL PRECAUTIONS

after some time. Soluble fluorides are toxic. By precipitating the fluoride ion as calcium fluoride the progress of the action can be stopped *e.g.* by subcutaneous administration of calcium gluconate lactobionate. Particular care should be taken that no hydrofluoric acid gets under the nails: this causes painful and prolonged inflammation.

## OTHER COMMON CHEMICALS

**Ammonia**—The vapours are pungent, suffocating, causing a burning throat, cough and strong irritation. In low concentrations the symptoms are similar to those of a severe cold. The solution exerts a local irritant action. In contact with the eye serious damage is produced, including lachrymation, burning sensations, and swelling of the eyelids, with pseudo-membranous lesions of the cornea and cataract formation in the lens.

**Hydrogen peroxide**—This causes burns which should be treated with hot water or with a solution of sodium thiosulphate; it is also a fire hazard in the presence of easily oxidizable material. The concentrated form is particularly dangerous.

**Heavy metals**—The vapours and many compounds of the heavy metals are very detrimental to health even in slight concentrations *e.g.* mercury, lead, arsenic, zinc, barium, chromates.

Substances of particular importance in the laboratory will be discussed separately.

## GENERAL PRECAUTIONS

Chemicals may cause damage in a great variety of other ways. We have already mentioned the explosion and fire hazards which accompany exothermic reactions. Sudden and violent reactions, such as occur when concentrated sulphuric acid is mixed with water, splashing or evolution of a gas *e.g.* of nitrogen oxides, must be watched constantly.

It is dangerous to look closely into a test tube or a flask, or to point the opening of a test tube towards a colleague; permanganate and sulphuric acid have already caused many serious accidents. It is unwise to blow into a wash bottle; when the pressure is released the contents may get into the mouth. An empty bottle must always be inserted between every two wash bottles containing chemicals which can react with each other.

Many chemicals can damage clothing: acids react with cellulose; wool is destroyed by alkalis. Clothes contaminated by an oxidant



such as nitric acid, nitrate or chlorate easily catch fire. Silver nitrate, tar and tar oils produce stains which are difficult to remove. It is extremely dangerous to neglect to take off clothes immediately which are soaked with a chemical or solvent. Some chemicals are rapidly absorbed by the skin and fatal poisoning may be the result of the neglect.

Chemicals which involve fire hazards *e.g.* phosphorus, carbon disulphide, sodium, potassium, strongly corrosive substances such as hydrofluoric acid, and very toxic substances should be stored only in small quantities. Several chemicals are so sensitive to moisture or to oxygen that they deteriorate once the bottle has been opened, by hydrolysis or oxidation or by reaction with carbon dioxide in the atmosphere. This applies for instance to the chlorides of phosphorus, silicon, aluminium, iron, titanium, tin and to alkali and ammonium sulphides and cyanides.

Such chemicals, as well as reagents of high purity, must always be stored in small bottles (see Table 32, p 208), preferably with a protective cap over the stopper.

## MERCURY

Mercury is a very toxic substance. Soluble mercury compounds produce severe acute poisoning. Mercury vapour even in extremely low concentrations, when inhaled regularly or periodically over a sufficiently long time, produces a slowly developing disease by reason of its cumulative effect. This more or less acute poisoning is characterized by digestive troubles and nephritis, and sometimes produces abscesses in the mouth and throat, bleeding of the gums, and loosening of the teeth.

The slowly developing chronic mercury poisoning is characterized by nervous disturbances such as tremor of the eyelids, fingers and tongue, jerky movements, and irritability. The patient, after recovering, often shows a supersensitivity to mercury.

A concentration of 1 mg of mercury in 10 cubic metres of air has been accepted by the American Standards Association as the maximum permissible concentration. One cubic metre of air saturated at room temperature with mercury vapour contains 15 to 20 mg (Table 9) ; consequently working with mercury in open vessels or spilling it should be avoided.

**Handling spilled mercury**—It is advisable to place any apparatus in which mercury is handled under an exhaust hood and in a wooden or enamelled iron tray, or on a bench provided with a projecting edge and a drain. The apparatus may also be placed in or over a tray containing a thin layer of water, the bottom of which is slightly

# MERCURY

Table 9. Vapour pressure of mercury and concentration in air at various temperatures

<i>Temp t</i> °C	<i>Pressure p</i> mmHg	<i>Mg Hg/litre</i>	<i>Parts per million</i>
20	0.0013	0.015	2
30	0.0029	0.034	4
40	0.0060	0.07	8.5
60	0.030	0.35	42.5
100	0.28	3.3	400
200	18.3	213	25,800
300	246	2,900	348,000

inclined and provided at the lowest point with a discharge device. Apparatus may break, a tube may burst or slip off, and mercury may be spilled. These precautions save the annoying and difficult task of collecting spilled mercury.

For this task mercury tongs are in frequent use ; the operation is rather time-consuming and ineffective. A mercury pipette is better ; this consists of a glass tube with a narrow thick-walled point. By connecting it with the vacuum line or with a suction pump the mercury is sucked into the tube, which is provided with a splash bulb and a reservoir to collect the mercury.

Small drops of mercury can be removed by rubbing with tin foil or with a small flattened spoon or spatula of amalgamated copper. Nickel-zinc amalgam is also recommended for collecting small drops of mercury. It is prepared by heating mercury, covered with some acetic acid, with one per cent zinc and adding a solution of a nickel salt until the liquid retains a green colour. The amalgam is then collected in a filter crucible and pressed out. It is kept under acetic acid<sup>1</sup>.

Frequently a worker is not aware that mercury has been spilled. With a tiled laboratory bench it has often been observed that in the course of time a considerable quantity of spilled mercury has assembled between cracks in the tiles. Mercury spilled on the floor should be covered with flowers of sulphur, by means of which it is converted to sulphide and thus rendered harmless. Mercury deposits can also be inactivated by treating them with calcium polysulphide, which combines with the mercury to form the sulphide and moreover encloses minute mercury droplets in a non-volatile envelope. Application of a chlorinated rubber lacquer or wax with 3 to 5 per cent of sulphur is also recommended, as well as cementing hard-surfaced linoleum to the floor<sup>2</sup>. It is, however, impossible to remove the mercury from the cracks in the floor, hence it is desirable that rooms where mercury is frequently being handled should be well ventilated and provided with a seamless floor.

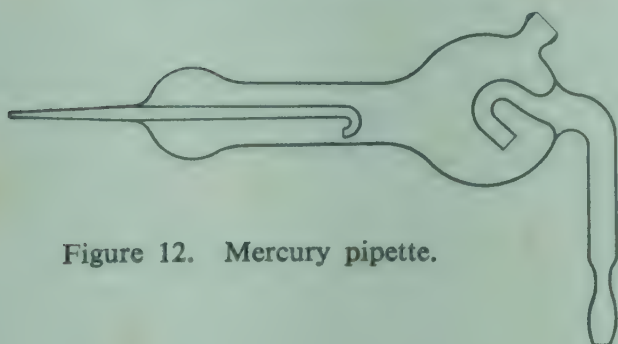


Figure 12. Mercury pipette.

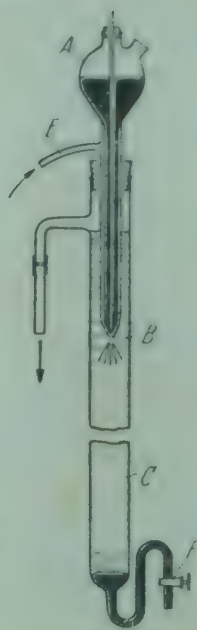


Figure 13. Apparatus for Cleaning Mercury.  
Tube *C* is filled with nitric acid (10 per cent). The mercury dropping in the tube at *B* is dispersed in the acid by a stream of air entering at *E*. The purified mercury is discharged at *F*.

**Mercury vapour**—The vapour escaping from an apparatus can be effectively absorbed in active carbon treated with bromine or iodine.

A case of mercury poisoning contracted during a determination of active sulphur in motor fuel has been described. In this determination the sample is heated with mercury and the sulphur converted into mercury sulphide. Finally the sulphur is reduced by nascent hydrogen. The hydrogen sulphide is swept out by a stream of carbon dioxide and collected in a solution of cadmium acetate. The apparatus in question was not placed in an exhaust hood, nor was the outlet protected by a tube containing active carbon and iodine, so that the stream of carbon dioxide charged with mercury vapour spread through the room and caused poisoning.

If mercury is used as a seal for stirrers, care should be taken that no mercury can be flung out. Mercury should not be used as a sealing liquid in a hot place. If possible the mercury should be covered with water or oil.

**Purification of mercury**—The usual methods for purifying mercury are :

- a* filtration through filter paper in which a small hole has been pricked
- b* passing through a column of benzene, alcohol or sodium hydroxide solution, if the mercury is contaminated with grease or oil



*c* treating with 2N nitric acid, followed by washing with water and drying, either by passing the mercury through a paper filter or by heating it to 150°C in a porcelain dish under a hood. This method of purification involves several hazards. If concentrated nitric acid is taken by mistake, a rather violent evolution of gas results. Diluted nitric acid also gives off nitrogen oxides which are very poisonous. In a closed separating funnel or in a closed flask they may cause considerable pressure, which can have very unpleasant consequences. Since mercury vapours are extremely poisonous it is advisable to leave the purification of mercury to experienced persons.

Apparatus for cleaning mercury is illustrated in Figure 13. The tube *C* is filled with 10 per cent nitric acid. The mercury dropping in the tube at *B* is dispersed in the acid by a stream of air entering at *E*. The purified mercury is discharged at *F*.

## INORGANIC COMPOUNDS

**Carbon disulphide**—Low boiling point, great toxicity and exceptional fire hazard make carbon disulphide an extremely dangerous substance. The laboratory worker would be well advised to keep it out of the laboratory as much as possible ; usually a less dangerous substitute can be found.

Carbon disulphide enters the body through the lungs where it is directly absorbed in the blood, and through the skin which is permeable to carbon disulphide. As a fat solvent it has narcotic properties. In acute cases patients complain of headache and become excitable, talkative and irritable. There may be giddiness, slow breathing and muscular weakness. These effects will dissipate in fresh air. In severe cases coma and death may supervene. Chronic cases are characterized by disturbances of the nervous system such as fatigue, dizziness, paralysis, disturbance of eyesight, even blindness, nervous symptoms, sleeplessness and loss of memory. There is practically no part of the nervous system which is not affected by it. Recovery takes a long time.

Carbon disulphide is secreted by the lungs, the kidneys and the skin. Ventilation and regular medical control are indispensable safety measures.

**White phosphorus**—This is very toxic. In chronic cases of poisoning there is a degenerative action on the bones. Necrosis of the jaw was an occupational disease in the manufacture of phosphorus matches : moreover phosphorus causes yellow atrophy of the liver, bleeding, and degeneration of the muscles. It should never be picked up with the fingers as it may cause serious and lasting burns.

**Arsenic**—The poisonous action of arsenic is due to paralysis of the capillary vessels. This causes an accumulation of blood in the abdominal cavity and a reduced blood supply to the organs, leading to characteristic disturbances of the stomach and intestines and affection of mucous membranes (eyes, nose cavities, pharynx, trachea) and of the skin (scaling, fading, falling out of hair, eruptions). The insufficient supply of blood to the nervous system causes headache, mental disturbances, troubled eyesight, insensibility of the extremities followed by paralysis, degeneration of the heart, liver and kidneys, and necrosis of fingers and toes.

**Arsine**—Arsine is formed wherever nascent hydrogen reacts with arsenic compounds. Many metals, as well as sulphuric acid prepared from pyrites by the lead chamber process and hydrochloric acid prepared with chamber acid, contain arsenic. Thus the reaction of acids with metals producing hydrogen is a potential hazard owing to the possibility of arsine formation. Several cases of poisoning during the cleaning of acid tanks, mostly fatal, have been reported. Another source of arsine is the action of alkalis on zinc containing arsenic.

Arsine is very treacherous. It can be breathed imperceptibly, since it does not irritate the air passages. It is absorbed by the blood and reacts with the haemoglobin, destroying the red blood corpuscles and causing oxygen deficiency.

The constituents and the decomposition products of the red blood corpuscles are secreted in the urine (damage to the kidneys is characteristic), and the secretion of bile is greatly stimulated, producing jaundice and affections of the liver.

**Lead**—Lead and most lead compounds are very toxic. Absorption takes place in the lungs, from lead vapour produced during soldering or welding, the dust of lead compounds from grinding, mixing and applying paints and glazes ; and with our food from contamination by dust or paint, or in soft water in contact with lead plumbing. Tetraethyl lead, the well known anti-knock compound contained in petrol, is absorbed by the skin.

Most of the lead absorbed in the blood is precipitated as phosphate in the bones, and redissolved each time the *pH* of the blood falls below a certain threshold value. This accounts for the cumulative action of lead compounds, which is responsible for chronic cases.

The characteristics of chronic lead poisoning are change of the white and destruction of the red blood corpuscles owing to damage of the bone marrow, leading to anaemia and a typical grey complexion in the patient ; dyspepsia (lead colic) ; painful joints ; nephritic diseases ; and nervous troubles such as trembling and paralysis.



**Potassium, sodium and ammonium chlorates**—Red blood corpuscles are destroyed by chlorates and the haemoglobin is oxidized to methaemoglobin, causing oxygen deficiency, jaundice, secretion of blood in the urine, thrombosis and nephritis.

**Chromic acid and chromates**—These interfere with cell metabolism and cause necrosis. They affect the mucous membranes of mouth, nose and throat, and cause perforation of the septum. They also damage the kidneys, the respiratory organs, giving bronchial catarrh, asthma and cancer. The skin is very sensitive to chromic acid and chromates, which can produce eczema.

**Fluorine**—Hydrofluoric acid is a poison with a strongly irritant action on the skin and the mucous membranes, forming painful blisters which heal very slowly.

The vapours of hydrofluoric acid cause irritation of the mucous membranes of the upper respiratory tract, secretion of mucous from the nose, a flood of tears, and fits of coughing blood. Sodium fluoride causes strong local irritations. Poisoning of plants and cattle have been observed in the neighbourhood of factories which allow fluorine to escape into the atmosphere. By feeding on plants containing fluorine, the cattle contract symptoms of fluorine cachexy, accompanied by pathological anatomical modifications in the bones.

Sodium fluoride causes stomach and intestinal troubles, excessive secretion of saliva and itching of the skin. Chronic cases have been described where the poison has been used as a preservative in food.

Silicon fluoride and hydrofluosilicic acid, which are applied as germicides, cause the same symptoms as hydrofluoric acid; sodium fluoride and sodium fluosilicate, both of which are used as disinfectants and insecticides, have the same effects.

Fluorine is a normal constituent of the body, especially the bones. Too much fluorine, however, is in general detrimental for bony tissues; in particular the teeth, which become brittle, with striped enamel.

Rubber gloves, proper protection of the respiratory system, and effective ventilation are the means of protection against hydrofluoric acid poisoning.

The typical action of fluoride ions on the organism is a result of their reaction with calcium ions. Hence, for the treatment of hydrofluoric acid blisters on the skin, aqueous or alcoholic solutions of calcium chloride are recommended, or a paste of calcium hydroxide or magnesia in glycerol. The hydrofluoric acid is thereby precipitated as harmless calcium fluoride. As first aid, dilution of the hydrofluoric acid by profusely flushing the affected parts with water is recommended. Injections of calcium gluconate or lactobionate are applied as antidotes in fluorine poisoning.



**Beryllium**—Beryllium may cause acute and chronic diseases of the lungs, and is also reported to have a delaying influence on the healing of wounds. The acute phase of the lung disease has been called acute pneumonitis of beryllium workers ; the chronic phase which has been described as a form of pneumokoniosis is a pulmonary granulomatosis. The acute reactions which may occur in the laboratory are dermatitis, conjunctivitis and irritation of the upper respiratory tract, with or without pulmonary oedema.

The chronic lesions of the lungs result in a thickening of the walls of the alveoli, thus causing dyspnea by diminishing the gaseous exchanges between air and blood ; the heart may be overburdened and insufficiency of the heart muscles may develop.

Such chronic cases have been diagnosed in workers engaged in the manufacture of fluorescent lamps. The application of fluorescent tubes for factory and domestic lighting purposes introduces this danger to the general public. It should be stressed that the burned out tubes have to be handled with great care so as to avoid cuts by broken fragments. Fluorescent lamp tubes are coated on the inside with a fluorescent powder containing 0.1 to 4 per cent beryllium. In 1948 there were reported cases of persons who had been cut by pieces of broken tubes and whose wounds were slow in healing. Care should be taken in disposing of used and broken tubes. When a person is cut by pieces of the glass he should be referred immediately to a doctor. First aid should consist in inducing the wound to bleed freely<sup>3</sup>.

MACHLE, BEYER and GREGORIUS<sup>4</sup> report cases which have occurred where the exposure to beryllium oxide exceeded 100 micrograms per cubic metre of air ; no cases are known to have occurred during six years of exposure to fluorescent compounds at levels of 2 to 8 micrograms per cubic metre of air.

Beryllium which is inhaled and retained in the lungs is gradually distributed widely through the tissues of the body. It is excreted only very slowly. In one example the lungs contained 20 micrograms of beryllium per 100 grams of tissue five years after the last exposure. The excretion at that time was less than 0.1 mg per day in the urine.

The major conditions associated with exposure to beryllium compounds are irritation of the eyes, nose and throat, dermatitis, subcutaneous granulomas and acute and chronic berylliosis. The first three conditions seem to be the result of exposure to soluble salts. The sub-cutaneous granulomas occur as the result of introduction of the material beneath the skin. The acute form of berylliosis may occur several months to six years after the termination of the exposure to beryllium compounds. It commonly starts with a

cough, loss of weight, increasing fatigability and weakness. The loss in weight and weakness are persistent and difficulty in breathing develops.

## ORGANIC COMPOUNDS

Hydrocarbons, alcohols, ethers and some esters have a narcotic action. Methyl esters and formic esters are lung poisons. Aromatic hydrocarbons, amines and nitro compounds are blood poisons. Chlorinated hydrocarbons are poisonous to the liver and kidneys. Moreover most organic solvents are skin irritants, causing eczema.

Regular handling of organic solvents constitutes a very positive health hazard. The most effective way to protect the worker is in the first place to keep those solvents as much as possible in closed containers, to perform operations in closed apparatus and to provide for ample and effective ventilation. Where the vapour density of an organic solvent is greater than that of air ventilation should preferably be at ground level. Cleanliness is imperative ; gloves, change of clothing before and after the work, and no food during work, are necessary. Protective creams are prohibited because of the dissolving action of the solvents. Instruction and education are of the greatest importance. Clothes which are contaminated with the toxic substance should be removed promptly.

### ALIPHATIC COMPOUNDS

**Hydrocarbons**—The light hydrocarbons have a narcotic action. Chronic poisoning by petroleum spirit is chiefly restricted to disturbances of the nervous system; moreover it irritates the mucous membranes and the skin.

**Alcohols and esters**—These compounds have a narcotic action. Methanol paralyzes cell metabolism and damages all kinds of organs and especially the nervous system, particularly the visual nerve, causing blurring of vision and even blindness. Methanol is absorbed *via* the stomach, the lungs or the skin. It is only slowly excreted from the body by the lungs and as formic acid by the kidneys, thereby causing degeneration of the kidneys.

**Acids and esters**—Glacial acetic acid irritates the skin and the mucous membranes of the mouth and the upper respiratory tract. It dissolves the blood corpuscles and affects the kidneys.

Oxalic acid affects the mucous membranes. When absorbed by the alimentary canal it is very poisonous because it eliminates calcium ions from the body liquids.

Dimethyl sulphate causes acute shortage of oxygen of the tissues owing to the formation of methaemoglobin. It irritates the skin and the mucous membranes, causing injury to the eyes, and is



extremely irritating to all parts of the respiratory tract, causing inflammation of the lungs and internal bleeding.

**Halogenated hydrocarbons**—As solvents for fats the halogenated hydrocarbons have a strong narcotic action and are absorbed by the skin. They damage various organs such as heart, lungs, liver, kidneys, adrenal glands, digestive and nervous system, and have an irritating effect on the skin.

They are dangerous poisons which may produce serious effects even when present in low concentrations. The susceptibility to the direct toxic effects is greater after the use of alcohol.

The symptoms of poisoning by chlorinated hydrocarbons are headache, dizziness, depression, fatigue, loss of appetite, nausea, vomiting and visual disturbances. In severe cases weak pulse, fever, blood in the urine, enlarged and painful liver, increase of the number of white corpuscles, low blood sugar and irritation of skin, eyes and respiratory tract occur. The action on the liver causes jaundice in chronic cases of chlorinated hydrocarbon poisoning. Protective devices made of ordinary rubber are permeable to chlorinated hydrocarbons ; neoprene should be used instead.

The use of halogenated hydrocarbons in fire extinguishing should be restricted to special occasions because of the dangers inherent in their toxicity.

Most chlorinated organic compounds when heated for a considerable time at or above their boiling point tend to decompose slightly and generate gaseous hydrogen chloride which is dangerous ; it is usually detected by its odour. The toxicity of some chlorinated hydrocarbons relative to chloroform is given in Table 10.

Table 10. Relative toxicity of chlorinated hydrocarbons\*

<i>Compound</i>	<i>Toxicity relative to chloroform</i>
<i>Ethyl chloride</i> ...	0.05
<i>Ethyl bromide</i> ...	0.06
<i>Methyl chloride</i> ...	0.2
<i>Trichlorethylene</i> ...	0.5
<i>Tetrachlorethylene</i> ...	0.5
<i>Chloroform</i>	1.0
<i>Carbon tetrachloride</i>	1.0
<i>Methyl bromide</i> ...	2.0
<i>Tetrachlorethane</i> ...	10.0

**Methyl chloride and bromide**—Methyl chloride has a slightly narcotic action, a strong irritating effect on the mucous membranes and causes damage to the lungs and eventually to the kidneys.

\*From HENDERSON, I. and HAGGARD, H. *Noxious Gases* p 202 New York, 1943



## ORGANIC COMPOUNDS

Inhalation of methyl bromide causes general disturbances such as headache, dizziness, and sickness. After some hours, sometimes after days, serious nervous disturbances occur *e.g.* cramps and disturbance of eyesight. If the patient does not die in coma the recovery will be prolonged and also the lungs may be affected as well as the skin. Hence there is every reason to be careful in using methyl bromide in fire extinguishers and refrigerators. The following example illustrates the typical effects of the toxic action of halogenated hydrocarbons.

A man engaged in fighting a fire with carbon dioxide and methyl bromide exhibited the signs of acute methyl bromide poisoning with subsequent development of uremia and impairment of renal function<sup>5</sup>. Delayed drunken sensations, giddiness, headache, epigastric discomfort, vomiting, and indistinct speech, numbness and tingling sensations of the feet, with smarting of the eyes, were the salient clinical features. Where methyl bromide has come into prolonged contact with the skin a burning sensation with delayed blister formation has been described<sup>6</sup>.

**Trichlorethylene**—This is much used as a solvent. It has the physiological properties typical of the halogenated hydrocarbons. At first the narcotic action causes a state of excitement or intoxication. Some persons even grow addicted to it. On the skin it forms blisters and finally eczema, owing to its fat dissolving properties.

Trichlorethylene particularly affects the nervous system and may lead to blindness, at the same time also interfering with the sense of touch. Of its other effects, irritation of the eye and affection of the respiratory and digestive organs are the most important.

## AROMATIC COMPOUNDS

**Benzene**—Benzene is rapidly absorbed in the lungs and distributed by the blood. As it is only slightly soluble in the body fluids only small amounts are absorbed by the body. Equilibrium, resulting in the establishment of a definite ratio between the concentration of benzene in the air, the blood and the tissues, is rapidly reached. The absorption is greatest and therefore more gradual in fatty tissues. Part of the benzene is oxidized to phenol and eliminated in the urine, combined with sulphate and glucuronic acid.

Benzene and its homologues have a definite narcotic action. They decompose enzymes and vitamins and cause lipomatosis of organs and internal bleedings. Even in low concentrations benzene is a blood poison. It affects the bone marrow, destroys the blood cells and makes the wall of the blood vessels permeable to blood constituents. The subjective sensitivity may vary within wide limits.

## HANDLING TOXIC AND INJURIOUS SUBSTANCES

Young persons are especially sensitive to chronic benzene poisoning. Regular medical inspection is essential. The skin absorbs benzene ; repeated contact of skin and benzene may cause eczema.

Acute benzene poisoning causes tightening of the leg muscles, dizziness, pressure on the forehead, confusion and a state of excitement (intoxication) followed by paralysis of breathing and of the heart.

Chronic poisoning is caused by repeated absorption of small quantities of benzene through the lungs or by the skin. Chronic benzene poisoning develops slowly ; it can be recognized as such only by close medical control and the damage in most cases is irreparable because of the persistence of the abnormal composition of the blood, even after the cessation of the exposure. These abnormalities are mostly progressive and irreversible.

The general symptoms of a chronic benzene poisoning are headache, depressed mood, fatigue, dizziness, bad appetite and loss of weight, bleeding of the mucous membranes of the nose and gums, irregular and excessive menstruation in women (who are exceedingly sensitive to benzene), and petechial bleedings of the skin. Pushing and pinching will cause blue spots owing to subcutaneous bleedings. The increasing pallor of the patient indicates anaemia.

All the above symptoms can be traced to the effects on the bone marrow, where most of the blood cells are made. The red corpuscles are destroyed and the production of blood platelets is interfered with ; this causes the bleeding of the skin and of the mucous membranes. The young blood cells do not come to full development, so that mature cells (erythroblasts and myelocytes) disappear (agranulocytosis). The number of white blood corpuscles is abnormal and generally low ; the final result is fatal.

The following blood counts (Table 11)\* have been described as typical indications of benzene poisoning :

Table 11. Blood counts typical of benzene poisoning

Type of cells	Number of cells per mm <sup>3</sup>
<i>White cells</i> ... ..	<5,000 or > 10,000
<i>Red cells</i> ...	<4 million
<i>Haemoglobin</i> ... ..	<80 per cent
<i>Platelets</i> ... ..	<100,000
<i>Polymorphonuclear leucocytes,</i> <i>appearance of immature blood cells</i> ...	<50 per cent

\*U.S Labour Dept. Controlling Chemical Hazards Ser. No. 6/1 Washington, 1946



**Abnormal blood counts** are an indication of a developing benzene poisoning. For this reason routine blood counts are indispensable, but diagnosis cannot be based on blood findings alone.

The elimination of benzene by the kidneys results in a lowering of the proportion of inorganic sulphate to total sulphate in the urine by ethereal sulphate excretion. This may give a definite warning before the chronic benzene poisoning has developed. Urine sulphate ratios below 70 per cent indicate harmful exposure to benzene, other factors which may depress this ratio being absent. Owing to the urinary excretion of ascorbic acid, persons working with benzene are more difficult to saturate with vitamin c.

**Toluene**—The toxic action of toluene is less than that of benzene and the xylenes are less dangerous than toluene. The action of the ascorbic acid level of the body is typical for toluene.

Toluene is oxidized in the body to benzoic acid, which combines with glycerol in the liver and is excreted as hippuric acid.

**Xylene**—Xylene is oxidized to toluic acid, only one methyl group being capable of oxidation, and excreted in the urine.

It has a stronger irritant action on the skin than benzene. For benzene a concentration of 100 ppm was accepted as the maximum allowable only a few years ago. Recently it was lowered to 50 and even to 35 ppm. The only absolutely safe consideration is zero.

**Nitro compounds**—Nitro compounds are very toxic. They may enter the body *via* the lungs, through the skin or with food, a rapid absorption by the skin being the most important and characteristic for these compounds. They have a paralytic action and act as blood poisons, causing formation of methaemoglobin and destruction of the red blood corpuscles. As a result of this haemolysis the red blood corpuscle count is reduced, the blood pigment is secreted in the urine (haemoglobinuria) and the secretion of bile is increased. The destructive action on the blood results in oxygen deficiency (anaemia) and jaundice. The changes in the blood are manifested by a typical chocolate-brown complexion and a bluish colour of the mucous membranes and skin. The oxygen deficiency is accelerated and accentuated by the detrimental effect of the nitro compounds on the metabolism of the cells, probably by their paralysing the oxidation enzymes.

They widen the blood vessels, irritate the gastro-intestinal tract and affect the skin, causing erythema. The widening of the blood vessels lowers the blood pressure and may result in collapse. Breathing is accelerated and deepened, the pulse becoming faster.

Recovery from poisoning by nitro compounds is slow. It is followed by protracted anaemia accompanied by jaundice and a



lasting weakening of the eyesight. The irritant action on the skin is typical and generally produces eczema. Subjective sensitivity may vary considerably.

Acute poisoning with nitro compounds is characterized by blue lips and nail beds, pallor, dark blood and urine, and a weak pulse. In such cases the patient complains of faintness and headache. Chronic poisoning is generally caused by absorption of small quantities through the skin or by inhalation of the vapour and is characterized by pallor, fatigue and mild anaemia.

Characteristic methaemoglobin producers are nitrobenzene, dinitrobenzene, trinitrophenol and the aromatic amines. Chlorination, as well as increasing the number of nitro groups in the molecule, increases the toxicity. The toxicity is decreased by introducing alkyl radicals, by sulphonation and by carboxylation.

The toxic effects of nitro compounds are accentuated by alcohol. Protection against such poisons is based on cleanliness, ventilation, application of personal safety devices (protective clothing, goggles, respirators) and periodical medical examinations including blood counts and the determination of the saturation with vitamin c. A regular supply of vitamin c is recommended.

Dinitrobenzene is very toxic and produces cyanosis and yellow atrophy of the liver. Alcohol and sunlight bring on a dramatic return of the symptoms. The poison enters the body by absorption of the compounds deposited on skin and clothing and in the lungs.

Tetranitromethane, a contaminant in crude trinitrotoluene, is highly toxic and irritating. It is formed in the nitration of toluene. It is volatile, has a pungent odour and a high surface tension, which increases its toxicity. Exposure to fumes of crude trinitrotoluene leads to irritation of mucosae, causing coughing, dyspnea and dizziness<sup>7</sup>.

The spectacular toxicity of such compounds as dinitrobenzene and dinitrochlorobenzene has been given the following explanation.

In the blood the nitro group is reduced to the hydroxylamine group :



This group links the compound to the haemoglobin which thereby is rendered inactive in regard to the oxygen transport.

With nitrobenzene the hydroxylamine is converted into *p*-aminophenol :



By chain reaction this is converted into non-poisonous substances which are excreted by the kidneys.

Dinitrobenzene is reduced in the blood to a compound with a hydroxylamine group, which reacts with the haemoglobin. The *m*-nitrophenylene-hydroxylamine, however, cannot be converted into the corresponding aminophenol owing to the presence of the second nitro group. Consequently the toxic effect of dinitrobenzene on the blood lasts much longer. Even after a slight poisoning with dinitrobenzene the recovery may take several weeks.

The following description<sup>8</sup> is illustrative for dinitrobenzene poisoning :

A man using a large vessel containing dinitrobenzene and boiling water developed headache, sleeplessness, paresthesia of the legs, diffuse pruritus and visual deterioration. He showed jaundice and mild cyanosis and enlargement of the liver. There was moderate anaemia and increased haemoglobin metabolism. In the hospital all symptoms subsided except the visual disturbances.

**Aniline**—Aniline may enter the body through the skin, through the lungs and through the digestive tract. It is a blood poison and interferes with the nervous system. Many derivatives of aniline have similar poisonous properties (methyl violet, nitraniline, dimethylaniline, diaminobenzene) and cause eczema *e.g.* *p*-phenylenediamine and asthma.

If the substance is resorbed from the stomach a few grams will have a fatal effect. Aniline is excreted by the kidneys as *p*-aminophenol.

Acute poisoning is soon followed by cyanosis, shown by pale blue lips, nose, ears and nails, often accompanied by a state of excitement. Progressive poisoning produces vomiting, headache, dizziness and hematuria. Acceleration of breathing and pulse, exhaustion, cramps, unconsciousness and death follow as the methaemoglobinemia progresses. Chronic poisoning is characterized by the destructive action of aniline on the blood, producing increasing anaemia. A low pulse rate and a high blood pressure are often encountered and sometimes the victim shows skin eruptions.

The symptoms are primarily caused by the formation of methaemoglobin, followed by degeneration of the red blood corpuscles. The poisonous action on the nervous system causes mental disturbances.

Handling aromatic amino-compounds, such as toluidine, dimethylaniline and especially  $\beta$ -naphthylamine and benzidine, may produce, even after many years, tumours of the bladder (papilloma). This affection may be treated by x-rays and by operative therapy. By regular urine control the initial pathological affections can be diagnosed. Alcohol increases the sensitivity to these substances.

Women and young males are more sensitive than adult males. A person who has recovered from an aniline poisoning remains more



sensitive than those who have not been affected. High temperatures and perspiration promote the poisoning.

**Phenols**—These are highly toxic protoplasmic poisons, especially characterized by their strongly corrosive action on the skin and the mucous membranes, by which they are readily absorbed.

**Phenol**—In the body phenol causes many serious derangements. It affects the nervous system, produces digestive disturbances, and may cause oedema of the lungs and degeneration of liver and kidneys. Serious phenol burns can produce gangrene and total necrosis. On prolonged contact *e.g.* continued exposure to dilute solutions, dermatitis is developed with local gangrene. Blond persons are especially sensitive. Phenol is excreted after oxidation or combination with acids. If the skin or the clothes are contaminated with phenols the soiled clothes should be removed at once and the affected parts of the skin flushed with warm water and washed with dilute alcohol. When working with phenols goggles should always be worn.

**Cresols**—These are protoplasmic poisons, less toxic than phenol. Poisoning results from contact of the skin with the irritant substance. Cresol may produce necrosis of the cornea, scars and even blindness. The skin burns may progress to ulceration. Chronic contact of the skin with cresols produces inflammation of the hair follicles, warty growths and spotty pigmentation. Systemic poisoning causes loss in weight, and damage to the liver and kidneys.

**Naphthols**—These compounds are much less irritant and toxic.

**Photographic developers**—Several phenol and amino compounds are used as photographic developers. They possess the poisonous properties of phenol *cq* aniline and are absorbed by the skin. These photographic chemicals should therefore be handled carefully. Developers should not be allowed to come into contact with the skin. Use stainless hooks or clamps and rubber gloves.

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## HANDLING TOXIC AND INJURIOUS SUBSTANCES

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## TOXIC GASES AND DUST

**M**ANY chemical reactions develop toxic gases (Table 37, p212). A laboratory worker handles several liquids, the vapours of which are toxic. The halogenated hydrocarbons used in fire extinguishers are also harmful.

The chemical worker should be aware of the gas hazard. He should be convinced that the human nose is not a reliable guide, subjective sensitiveness varying considerably, and some of the most dangerous gases and vapours having no smell at all or even an agreeable smell. Moreover, the human nose quickly loses its sensitivity under continuous stimulation.

Nitrous fumes are hazardous even at a concentration which is not detected by smell or by any irritation of the throat. On the other hand some noxious gases are so aggressive that the human body is stimulated to instantaneous reaction (chlorine, sulphur dioxide, hydrochloric acid, ammonia). Most gases have an insidious action and the body is not warned of their attack, hence it is necessary to know the action of such vapours upon the human body. The symptoms of chronic poisoning by gases being only revealed as such after a long time, it may be difficult to convince the worker of the danger. Chemical warfare in 1914-18 contributed much towards our insight into the mechanism of poisoning of human beings by gas and in developing means of detection and protection.

To eliminate poisoning by gases or vapours, care must be taken to avoid inhaling them even in low concentrations and for a short time. If the work cannot be performed in the open or in a room where the gases or vapours are removed by adequate ventilation, a suitable protective device should be worn.

Solvents should be used as much as possible in closed containers and closed apparatus : solvent-saturated rags should be deposited in closed metal containers. If symptoms of dizziness, headache or digestive troubles are felt, medical advice should be sought at once.

Gases enter the human body with the inhaled air. Some, such as halogens and halogenated hydrocarbons, lachrimators, mustard gas, hydrogen sulphide and many organic compounds, irritate the eyes; some penetrate the unprotected skin. When the gas is inhaled it may produce a corrosive action on the mucosae of the mouth, nose and throat and of the air passages and lung alveoli.



Typical examples of such primary irritants, the action of which is mainly restricted to the upper respiratory tract, are aldehydes (formaldehyde, acetaldehyde, acrolein), ammonia, alkali dust, hydrochloric acid, hydrofluoric acid, sulphur dioxide and sulphur trioxide, chromic acid. Substances which are not only strong irritants of the upper respiratory tract but which also penetrate into the lungs are chlorine, bromine, phosphorochlorides, dimethylsulphate.

Some of the most dangerous gases such as  $\text{AsH}_3$ ,  $\text{COCl}_2$ ,  $\text{NO}_2$  lack this corrosive action on the upper respiratory tract and primarily affect the terminal respiratory passages and the alveoli, producing oedema of the lungs by making the walls of the lung alveoli permeable to the blood plasma. The lungs are filled with liquid from the blood so that the patient is drowned in his blood plasma and may die by suffocation.

Other groups of noxious gases and fumes are dissolved in the blood. Some of them make the blood unable to transport oxygen, others alter the composition of the blood. Moreover the blood is a very efficient means of transporting the poison.

Hydrocyanic acid and arsine are distributed over the body tissues in a very short time, where they disturb the metabolic process of the cells or even bring it to a stop. Organic solvents in which fats are easily soluble have an effect on the nervous system, this being rich in lipoids, and in general therefore such solvents have a narcotic action. In addition they have a specific action, determined by their chemical properties. Therefore many narcotics may cause chronic disturbances of several organs. (Table 39, p 216)

The organo-metallic compounds which can penetrate the body as a gas or as a liquid are severe poisons *e.g.* tetraethyl lead, diethyl mercury, ethylmercury chloride, carbonyls and organic arsenic compounds.

Some poisons dissolved by the blood in the air passages and the lungs and transported through the body disturb the organs of metabolism (halogenated hydrocarbons); others damage the organs of excretion, especially urinary organs (glycol, ethyl tetrachloride), and some damage the bloodforming organs (benzene).

Carbon disulphide, methyl alcohol, ethylene trichloride and tricresyl phosphate are specific poisons of the nervous system.

The individual sensitiveness for poisons may differ very markedly. The resorption, transport and effect on the tissues and the excretion of those poisons depend on their concentration, vapour pressure and solubility in water, blood and fats. The result is determined by the chemical properties of the poison or by the properties of its decomposition or reaction products. These secondary poisons may give rise to chronic diseases.

## EXAMPLES OF TOXIC GASES

The velocity of the absorption by the blood of a gaseous contaminant present in the air in a given concentration gradually diminishes. Finally some kind of equilibrium is attained in which the concentration of the toxic gas in the blood has become constant. The process is determined by the partial pressure of the contaminant in the air, its solubility in the blood and in the other body fluids and organs, and the reactivity of the poisonous substance. When solubility and reactivity are slight, equilibrium is reached in a comparatively short time. With soluble and reactive gases this time is much longer. The same factors determine the velocity with which the contaminant is eliminated by the respiration process, Figure 14.

Some gases have no specific toxic properties but are noxious in high concentrations by reducing the partial pressure of the oxygen in the inhaled air, thereby causing oxygen deficiency.

It is necessary not only to be informed of the dangers of toxic gases but to be able to find out, in an objective way, if the air which we are breathing is safe. Fortunately, simple and quick methods are available for detecting noxious gases and fumes even in minute quantities or low concentrations. Colorimetric methods such as those published by the Department of Scientific and Industrial Research in London enable this detection to be performed with sufficient accuracy.

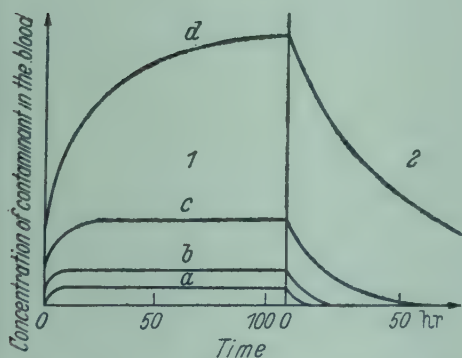


Figure 14. Diagrammatic representation of some types of saturation 1 and elimination 2 curves for different types of contaminant: *a* non-reactive, slightly soluble ( $N_2$ ), *b* moderately reactive, slightly soluble ( $CS_2$ ), *c* slightly reactive, moderately soluble ( $C_6H_6$ ), *d* slightly reactive, highly soluble ( $CH_3OH$ ). The concentration of contaminant in the atmosphere is  $x$  ppm.

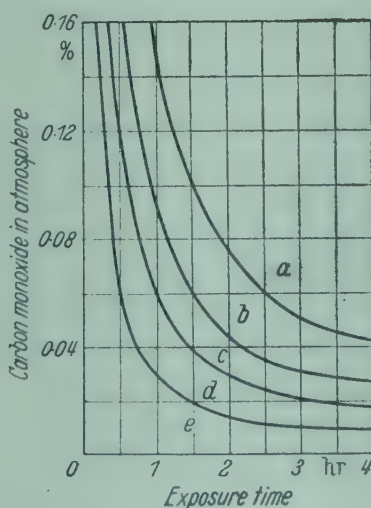


Figure 15. Effects of CO acting for a given time on human beings, from *Bureau Stand. (Wash.) Tech. Paper No. 212*. *a* fatal, *b* dangerous, *c* headache and nausea, *d* perceptible effects, *e* no perceptible effects.



## TOXIC GASES AND DUST

The sample of polluted air is led through a reagent by means of a hand pump. The reagent is used either as an absorbing solution or impregnated on a test paper. By determining the quantity of air that has to be passed through the reagent to produce a definite colour reaction, one can not only detect the noxious gas but also estimate its concentration.

When working with poisonous gases or with substances that can produce such gases, a well constructed fume hood should be used or the work carried out in the open air.

When by any chance the noxious gas is distributed in the working space, a respirator with the proper canister, or a self-contained breathing apparatus should be worn. All persons working in a toxic atmosphere should wear gas protecting devices and no person should be allowed to enter the area unprotected.

### CARBON MONOXIDE

Carbon monoxide occupies a special and rather prominent place amongst the toxic gases. On the one hand it is highly toxic and on the other it is of such general occurrence that practically everybody has something to do with it. It is of such wide occurrence because carbon monoxide is formed as the product of incomplete combustion of carbon and carbon compounds. Carbon monoxide is present in smoke and in the gases produced by a burner which has flashed back, in a luminous flame, or a flame in contact with a cold surface, in an electric furnace with carbon electrodes or charged with pulverized carbon, and in the exhaust gases of an internal combustion engine. It is a component of many industrial gases *e.g.* town gas, water gas, producer gas and blast furnace gas.

Carbon monoxide has a treacherous action because it gives no warning, being odourless and tasteless. It has about the same specific gravity as air. Slight concentrations which are already very poisonous are difficult to detect, to absorb or to render harmless. The effects of exposure for different periods at different concentrations are given in Figure 15.

The poisonous action is based on the affinity to haemoglobin with which it forms a relatively stable compound. The affinity of haemoglobin for carbon monoxide is 300 times its affinity for oxygen, with the result that even a slight concentration of carbon monoxide in the air may cause a considerable part of the haemoglobin to be blocked by carbon monoxide. This haemoglobin thereby loses its oxygen carrying capacity, with the result that the oxygen supply to the body is endangered. The ensuing oxygen deficiency has severe consequences. The first symptoms (Table 12), are headache, dizziness and weakness. When the oxygen deficiency

## CARBON MONOXIDE

is prolonged the nervous system and blood vessels are irreparably damaged. Serious intoxications with carbon monoxide produce unconsciousness, cessation of breathing, and death.

Table 12. Effects of CO Poisoning

<i>Total haemoglobin saturated with carbon monoxide per cent</i>	<i>Effects</i>
10	<i>None</i>
20	<i>Shortness of breath during physi- cal exercise</i>
30	<i>Dizziness, dyspnea</i>
40	<i>Dangerous</i>
over 40	<i>Fatal</i>

The percentage of the total haemoglobin saturated with carbon monoxide is a function of the concentration of the carbon monoxide in the atmosphere, the time during which this air is breathed and the inhalation volume per minute. The velocity with which the carbon monoxide is absorbed by the blood gradually diminishes, depending on the partial pressures of oxygen and carbon monoxide in the atmosphere and the relative affinities of these gases for haemoglobin.

$$\frac{[\text{HbCO}]}{[\text{HbO}_2]} = \frac{300p_{\text{CO}}}{p_{\text{O}_2}}$$

The degree of saturation of the haemoglobin with carbon monoxide is :

$$\frac{\text{HbCO}}{\text{Hb}_{\text{total}}} = \frac{p_{300\text{CO}}}{p_{\text{O}_2} + 300p_{\text{CO}}}$$

When the atmosphere contains *e.g.* 0.2 per cent by volume of CO and the alveolar air 15 per cent by volume of oxygen, the degree of saturation of the haemoglobin with CO in the equilibrium will be:

$$\frac{0.2 \times 300}{15 + 0.2 \times 300} = \frac{60}{75} = 80 \text{ per cent}$$

with 0.02 per cent by volume of carbon monoxide this figure will be :

$$\frac{0.02 \times 300}{15 + 0.02 \times 300} = \frac{6}{21} = 29 \text{ per cent}$$

With the aid of this equation the data of Table 13 have been obtained:



# TOXIC GASES AND DUST

Table 13. Combined haemoglobin at different carbon monoxide concentrations

<i>Volume per cent CO in atmosphere</i>	<i>Hb combined with CO per cent</i>
0.01	17
0.02	29
0.05	50
0.1	67
0.2	80

From this table we conclude that a 20 per cent saturation of the haemoglobin with carbon monoxide, already causing definite symptoms, a concentration over 0.01 per cent carbon monoxide is harmful and concentrations upwards from 0.05 per cent are dangerous.

When the blood which has reached equilibrium in contact with air containing carbon monoxide at a partial pressure of  $p_{CO}$  is treated with pure oxygen, the equilibrium is upset and carbon monoxide is eliminated from the blood because it is being replaced by oxygen, the saturation value of the haemoglobin with carbon monoxide in the presence of oxygen being much lower than in the presence of air as can be calculated from the above equation.

With air containing 0.2 per cent carbon monoxide the saturation value is 80 per cent. With oxygen it becomes :

$$\frac{0.2 \times 300}{100 + 0.2 \times 300} = \frac{60}{160} = 37.5 \text{ per cent}$$

Starting with 0.02 volume per cent carbon monoxide we find in the presence of pure oxygen  $\frac{0.02 \times 300}{100 + 0.02 \times 300} = 5.9$ , instead of 29 per cent in the presence of air.

The reversibility of the equilibrium :



therefore indicates that the absorbed carbon monoxide may be expelled from the blood by the administration of oxygen.

## CARBON MONOXIDE

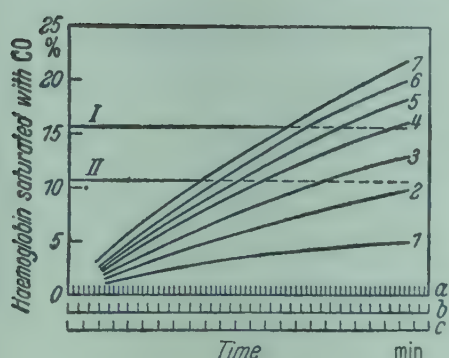


Figure 16. Rate of absorption of carbon monoxide in the blood *a* at rest, *b* walking, *c* working, *I* admissible limit for short period and *II* for long period : from DAUTREBANDE. The number on each curve gives the volume of CO per  $10^4$  volumes of air.

With low carbon monoxide concentrations there is a relationship which expresses the fact that the longer the contaminated air is breathed, the more serious is the effect (Table 14) where  $t$  is the time in hours during which air containing  $c$  ppm of carbon monoxide is breathed :

Table 14. Toxicity of Carbon Monoxide

<i>Effects</i>	<i>tc</i>
<i>None</i> ... ..	300
<i>Shortness of breath at exertion</i> ... ..	600
<i>Dizziness, oppression</i> ...	900
<i>Dangerous</i> ... ..	1,500
<i>Unconsciousness</i> ...	Over 1,500

Substitution of  $t = 1$  and  $t = 8$  hours gives the following result :

Table 15. Symptoms of Carbon Monoxide Poisoning

<i>Effects</i>	<i>Per cent CO in atmosphere</i>	
	<i>t = 1 hr</i>	<i>t = 8 hr</i>
<i>None</i> ... ..	0.03	0.004
<i>Shortness of breath during exercise</i>	0.06	0.008
<i>Dizziness</i> ... ..	0.09	0.011
<i>Dangerous</i> ... ..	0.15	0.020

Substitution of short times versus high concentrations is not allowed, the relation being applicable only approximately to low concentrations and long exposures.

The results of experiments and of cases of carbon monoxide poisoning have been summarized in Table 16.



# TOXIC GASES AND DUST

Table 16. Carbon Monoxide Poisoning Data

<i>CO in the atmosphere per cent by volume</i>	<i>Time of exposure min</i>	<i>Effects</i>
0.004	480	<i>None</i>
0.01	480	<i>Dizziness</i>
0.02	480	<i>Dangerous</i>
0.03	60	<i>None</i>
0.1	60	<i>Dizziness</i>
0.16	20	<i>Dizziness, headache</i>
0.16	60	<i>Dangerous</i>
0.32	5—10	<i>Dizziness, headache</i>
0.32	30	<i>Dangerous</i>
0.64	1—2	<i>Headache, dizziness</i>
0.64	10—15	<i>Dangerous</i>
1.28	1—3	<i>Fatal</i>

The equilibrium which is adjusted in the blood by the respiration of air containing carbon monoxide is attained more rapidly by increasing the respiratory volume *e.g.* as the result of exertion (Figure 16) or in the presence of carbon dioxide.

When the victim of carbon monoxide poisoning becomes aware of the danger he is generally no longer able to rescue himself. Besides, effort only aggravates the poisoning as a result of the more intensive respiration which this exertion would require.

The basic metabolism being proportional to the surface of the body, a certain degree of saturation of the blood with carbon monoxide is attained much more rapidly with small individuals, such as birds and mice. This principle underlies the use of canaries for the detection of carbon monoxide in coal mines. The method is however not dependable and cannot be recommended. Only an analysis gives definite information.

Since the symptoms of a carbon monoxide poisoning show that it is the result of oxygen deficiency, they may suggest a great many other causes, and the diagnosis cannot be given with certainty until the carbon monoxide has been detected in the blood. Allowance should be made for the fact that the blood of smokers invariably contains a considerable quantity of carbon monoxide.

# CARBON MONOXIDE

Table 17. Effect of Smoking on Haemoglobin

<i>Cigarettes smoked per day with inhalation</i>	<i>Haemoglobin saturated with carbon monoxide per cent</i>
<i>Over 30</i>	10
<i>20—30</i>	8
<i>10—20</i>	4
<i>10 or less</i>	2
<i>Cigars per day</i>	
<i>4 to 8</i>	10—20
<i>3 or less</i>	6—10

The production of carbon monoxide in the smoke of cigars, cigarettes and pipes depends on the velocity with which the tobacco is consumed. Rapid, nervous smoking, especially when combined with inhalation of the smoke favours intoxication with carbon monoxide. Some data are given in Tables 17 and 18.

Table 18. Carbon Monoxide produced by Smoking at Different Rates

<i>Type of tobacco</i>	<i>Tobacco gm/hr</i>	<i>Smoke contains</i>		<i>cm<sup>3</sup>CO per gm tobacco</i>
		<i>Per cent CO<sub>2</sub> by volume</i>	<i>Per cent CO by volume</i>	
<i>Cigarette</i> ...	4	4	0·6	4
	6	6	1	15
	7	9	3	30
	15	8	5	46
<i>Cigar</i> ...	4	8	1	11
	14	12	4	35
<i>Pipe</i> ...	6	16	0·5—1·5	10—30
	12	16—17	1·5—3·5	25—54

As far as we know carbon monoxide does not exercise a detrimental effect on the body cells.

Animals which had been exposed to an atmosphere with a high carbon monoxide content showed no detrimental effects when the pressure of the air was so much increased that the quantity of oxygen dissolved in the plasma was sufficient to supply the needs of the tissues. Animals in which the oxygen is not transported by haemoglobin live unharmed in an atmosphere containing a high carbon monoxide content, provided that sufficient oxygen is available.

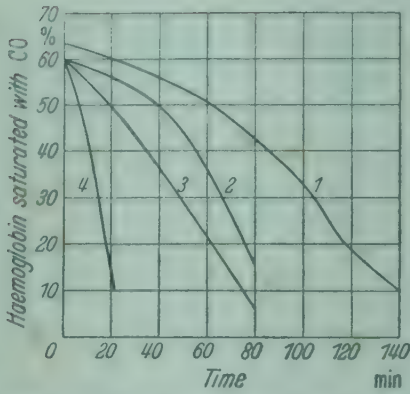


Figure 17. Elimination of carbon monoxide from the blood by 1 air, 2 oxygen, 3 air and carbon dioxide, 4 oxygen and carbon dioxide, according to DAUTREBANDE.

**First aid**—The patient should immediately be removed into the fresh air. The rescue party must be careful not to enter the poisoned atmosphere unprotected but to use self-contained breathing apparatus. After the patient has been removed to fresh air it is advisable to get him to bed. His clothing should first be removed entirely and if at all practicable any chemicals should be removed from his skin. It is inadvisable to put the patient in bed with hot water bottles unless his clothes have been removed, because any chemicals present on his clothing may be vaporized and their absorption through the skin, or their corrosive effect on it, will be accelerated. Oxygen should be administered at once. If respiration has ceased the administration of oxygen must be combined with artificial respiration.

Some doctors prefer to administer a mixture of oxygen with 5 to 7 per cent of carbon dioxide. The carbon dioxide helps to restore the natural respiration by its action on the respiratory centre. Figure 17 shows the rate of elimination of the carbon monoxide by different mixtures of gases. Figure 18 shows the changes in depth of respiration in a case of carbon monoxide poisoning when oxygen and carbon dioxide were given.

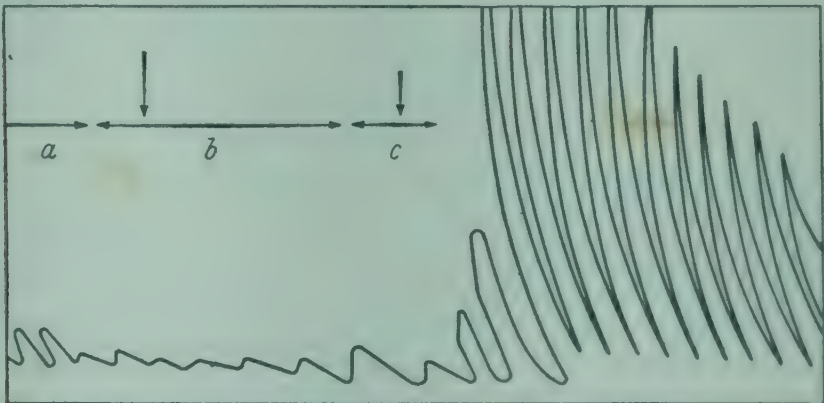


Figure 18. Depth of respiration in carbon monoxide poisoning a with serious CO poisoning ; b after administration of oxygen and c after administration of carbon dioxide (DAUTREBANDE).



**HYDROGEN SULPHIDE AND HYDROGEN CYANIDE**

**Hydrogen sulphide**—This is a very poisonous gas. Large concentrations are fatal and small concentrations cause serious disturbances of the gastro-intestinal tract. It is a blood poison. Although low concentrations of hydrogen sulphide have a very disagreeable odour, after a relatively short exposure or in higher concentrations the sense of smell rapidly becomes temporarily dulled and useless.

The irritation of the eyes degenerates into a painful conjunctivitis and keratitis. Protracted exposure to concentrations just over some tenths of a milligram of hydrogen sulphide per litre of air produces oedema. In addition to conjunctivitis, chronic hydrogen sulphide poisoning may cause headache, fatigue and gastro-intestinal troubles, while the skin becomes rough. Hydrogen sulphide acts on various enzymes so that the metabolism of the cells is lowered.

**Hydrogen cyanide and the cyanides**—These compounds, as well as a great many other cyanogen compounds *e.g.* calcium cyanamide, are very poisonous. Hydrogen cyanide and cyanides may enter the body through the lungs, the mouth and through the skin.

Examination of test animals revealed that after poisoning with hydrogen cyanide the oxygen contents of the venous blood and of the arterial blood were practically equal. This proved that there was sufficient oxygen in the blood but that the action of the hydrogen cyanide makes the cells unfit to combine with this oxygen, because of damage to the oxidation enzymes.

The final result is internal suffocation. Poisoning proceeds very rapidly. It mostly causes a reflex cessation of the heart action so that first aid generally comes too late. In order to eliminate the effect of hydrogen cyanide on the oxidizing process intravenous injections of methylene blue are applied (50 ml of a 1 per cent solution).

The cyanide ion is rapidly converted into cyanate and by the reaction with the albumins to thiocyanate ions. In order to promote this detoxication injections of colloidal sulphur or sodium thio-sulphate are recommended.

**SUFFOCATING GASES**

Examples of suffocating gases are chlorine, phosgene and nitrogen oxides. Inhalation of these gases may cause pulmonary oedema. The liquid which accumulates in the lungs originates from the blood. If the patient survives the crisis this liquid is gradually resorbed and recovery is complete.

**Phosgene**—Air contaminated with phosgene may be inhaled for some time without producing perceptible reactions. In this latent stage

the patient does not reveal symptoms of disease, neither does the objective examination give any indications, so that a poisoning is difficult to diagnose in an early stage.

After about two hours the respiration changes : frequency increases, and intensity decreases. This is caused by the secretion of liquid in the lungs leading to pulmonary oedema which rapidly reduces the active volume of the lungs.

A characteristic of this liquid is that, unlike pus or blood, it does not contain cells. It accumulates in the alveoli, which puts a greater strain on the muscles of the respiratory system and causes a sensation of progressive oppression.

As the available lung space decreases an increasing oxygen deficiency is created which results in unconsciousness and a highly accelerated respiration of very slight depth.

*First aid*—Originally artificial respiration used to be applied, which accelerated the secretion of liquid in the lungs, thus promoting a fatal issue of the process. Afterwards the progress of the poisoning was studied and the treatment accordingly adapted.

Primarily the patient needs absolute rest. Unnecessary movements increase the oxygen want and aggravate the oedema. As in the initial stage phosgene poisoning cannot be diagnosed, one can hardly be careful enough. Therefore the patient should be transported in a lying position ; unnecessary movements should be prevented.

In addition to rest first aid should consist in the administration of oxygen instead of air so that the active surface of the lungs is utilized as much as possible.

A uniform temperature is beneficial, hence adequate cover and hot water bottles should be provided to prevent muscular activity of the skin. Owing to the tissues secreting liquid the patient gets thirsty, but he should not be allowed to drink excessively because too much liquid aggravates the pulmonary oedema.

The oedema contains fibrine by which it is rendered gelatinous. It cannot be removed mechanically. In a later stage the oedema will contain blood cells so that the danger of inflammation of the lungs becomes imminent. It is characteristic of phosgene poisoning that only the alveoli are affected ; the epithelium of nose, throat and trachea remains intact.

The liquid which accumulates in the lungs is derived from the blood. This results in a considerable concentration of the blood, the number of cells augmenting from 5 or 6 to 10 million per mm<sup>3</sup> which means that one half of the plasma has been withdrawn from the blood circulation. The thickening of the blood constitutes an increased effort of the heart, which is still further accentuated owing



to the obstruction in the alveolar capillaries, so that there is a danger that the heart will not stand the strain. The thickening of the blood may also cause thrombosis. It can be prevented by administering an isotonic salt solution : after an hour, however, this solution will have lost its effect. Bleeding is more effective (500 to 1,000 ml). The body reacts on the sudden loss of blood by replenishing it with water withdrawn from the tissues. This liquid does not contain cells, albumens or other blood thickening substances. The restoration of the loss of blood cells begins only after about 24 hours.

**Chlorine**—Chlorine is a primary irritant. It causes violent coughing spasms and nausea. It produces hydrochloric acid which irritates the epithelium of the mucous membranes, thereby favouring secondary infections. The irritation results in a kind of pertinaceous bronchopneumonia.

As slight concentrations of chlorine (0.014 mg per litre of air) give adequate warning by smell, and higher concentrations strongly irritate the upper respiratory tract, chlorine poisoning is of rare occurrence.

Chronic cases are characterized by bronchitis, affections of the eyes, gastritis and sleeplessness.

In a concentration of 0.3 mg per litre of air it is already intolerable; 0.002 mg per litre of air is permissible.

The following description<sup>1</sup> is typical of chlorine poisoning:

After the immediate irritation the symptoms were confined to the respiratory tract. All patients had trachea bronchitis. Pulmonary oedema was present in 23 of 30 cases. In 14 pneumonia developed.

**Sulphur dioxide**—Sulphur dioxide is a primary irritant to the respiratory passages and the eyes. In relatively high concentrations it is suffocating. One gets used to small concentrations, which however impair the sense of smell and taste and may produce exertional dyspnea, fatigue and chronic bronchitis. Concentrations upwards from 20 ppm may cause respiratory tract inflammation and bronchitis.

**Nitrogen oxides**—These nitrous fumes are most hazardous. They can develop unexpectedly *e.g.* when a bottle containing nitric acid breaks, or when nitric acid comes into contact with organic substances such as sawdust. They may also be formed when metals are cleaned or etched with dilute nitric acid or when metals are galvanized or welded. Nitrogen oxides constitute a definite hazard in many chemical works, for instance, in the manufacture of nitric acid, sulphuric acid, ammonium nitrate, explosives or in the exhaust gases of diesel engines and in welding fumes.



## TOXIC GASES AND DUST

Slight concentrations of nitrous fumes although detrimental have no immediate and marked effect. A few minutes' exposure to a concentration of 1 in 1,000 parts by volume of air may have fatal results. Such dangerous concentrations do not give warning because they do not cause respiratory reflexes. Figure 19 shows the effect of exposure to  $\text{NO}_2$  on cats.

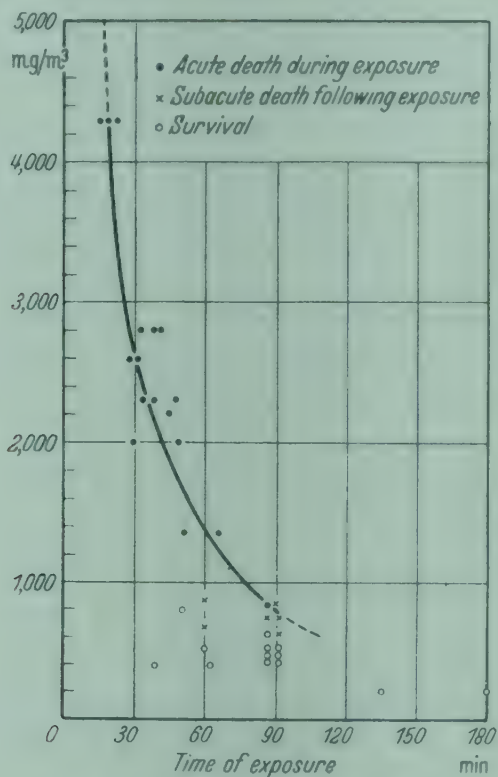


Figure 19. Toxicity of NO<sub>2</sub> for cats showing relationship between mean time of acute death and concentration of NO<sub>2</sub> in air (WIRTH).

An atmosphere in which nitrogen oxides can be detected by the smell must be considered as very dangerous.

The reaction of nitrogen oxides with moisture causes nitrous and nitric acids to be formed in the mucous membranes of the respiratory organs, which exercise a strongly irritant effect on the epithelium, producing a burning sensation in the throat, and coughing. The damage done to the alveolar cells results in oedema which involves the hazard of suffocation. The action on the blood is shown in the formation of methaemoglobin. As methaemoglobin is unfit for oxygen transport, oxygen deficiency *i.e.* cyanosis, results. The body reacts by accelerated production of red blood cells. Other organs are affected also *e.g.* heart, liver, and kidneys.

## DUST

Oedema is responsible for the fatal cases. Repeated inhalation of nitrogen oxides in slight concentrations gives rise to serious chronic effects.

*First aid*—Inhalation of nitrogen oxides may be continued for eight hours or more without poisoning symptoms being revealed. Hence the treatment is entirely similar to that of phosgene poisoning : absolute rest, administration of oxygen, bleeding. Inhalation of 0.03 mg per litre of air for a few hours is permissible. A concentration of 0.3 mg per litre of air is already dangerous at a few minutes' exposure.

## DUST

In various operations such as crushing, grinding, screening and glazing, dust is developed which is a hazard for our health.

A considerable quantity of the dust which is inhaled with the air we breathe is filtered out and cleared away by the nose. The mucous membranes of the trachea and bronchi are lined with cells provided with cilia by which dust particles not retained in the nose are whipped upwards. They subsequently are removed with the mucus by coughing. The finest particles penetrate into the alveoli. This means that invisible dust is the most dangerous. Experiments by WILSON and LA MER<sup>2</sup> with radioactive tracers indicated that of an aerosol the particles of 0.2 to 1.0  $\mu$  are most likely to reach the alveoli and up to 45 per cent of the dust contained in the inhaled air can be retained by the lungs.

It is not advisable to overtax the dust-filtering capacity of the nose and upper respiratory tract ; the spreading of dust should be avoided as much as possible.

The minute particles which have penetrated into the alveoli meet another natural defence system. The walls of the alveoli are lined with flat cells. Through the spaces between those cells phagocytes can pass. They engulf the foreign bodies and carry them through the wall of the tissue into the blood capillaries, enter the bronchioles, whence they are moved upwards by the cilia, enter the lymphatic system, and pass with the lymph through the lymph nodes, where the dust particles are retained.

The natural defence system breaks down when the atmosphere is relatively overloaded with dust or when the dust has special irritant or poisonous properties. The inert dusts weaken the defence system against dust and infections such as bronchitis and tuberculosis. Toxic dusts (metal fumes, lead and chromium compounds) produce systemic poisoning.

Organic dusts such as pollen, resins and wood, may produce allergic reactions, such as hay fever or asthma. Irritant substances

## TOXIC GASES AND DUST

e.g. alkalis, fluorides, chromates, may affect the mucous membranes of the upper respiratory tract, causing inflammations and promoting infections by pneumococci. Chromates are very hazardous and may even lead to the development of lung cancer.

Silica, several siliceous dusts and asbestos produce a typical reaction of the lung tissue by which this is replaced by scar tissue. The process is called fibrosis. It is not improbable that the reaction, which is typical for silica, is a result of the appreciable solubility of silica in the body fluids, the dissolved silicic acid having a destructive action on phagocytes and living cells in general, flocculating the albumens.

The symptoms of lung fibrosis develop gradually. The scar tissue embedding the foreign particles gradually builds up a network of inert tissue which more and more fills up the free space of the lungs. The breathing capacity of the lung thereby diminishes considerably and this invalidates the victim<sup>3</sup>.

The subjective sensitivity to dust in general and to siliceous dust in particular may vary considerably. The victim of 'dust-lungs' is more susceptible to infections such as bronchitis, pneumonia, and tuberculosis of the lungs.

Dust is not only hazardous for the respiratory system, but also for the eyes and sometimes for the skin. Moreover organic dusts present a considerable fire hazard. Therefore prevention and elimination of dust should always be aimed at.

**Dust prevention**—Dust should be removed at the source by applying closed systems and enclosures, local exhausts and wet methods of grinding.

For personal protection goggles, air line respirators and dust masks should be available. The filtering effect of a dust mask and its resistance to breathing are opposite factors. Dust masks have been developed which in both respects are reasonably satisfactory. The air line respirator gives the most satisfactory personal protection.

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## PROTECTIVE DEVICES AND FIRST AID

**P**ROTECTIVE devices, adequately designed and properly used, are a great help in preventing accidents or minimizing their effects.

**Ventilation**—The ventilation system is of the utmost importance in reducing the discomfort and hazard of poisoning caused by the inhalation of toxic gases.

The general ventilation system should provide the worker with pure conditioned air in such quantity that the concentrations of contaminants are kept below the accepted limit established for continuous exposure. Generally this can only be realized efficiently when in addition the contamination is controlled at the source, preferably by choosing safe conditions and methods. If however the evolution of toxic or irritant gases, fumes, mists or dusts cannot be avoided, spreading of irritant or toxic substance must be controlled by mechanical means, such as isolation, enclosure, special ventilation. If this is impossible in emergencies, personal protection becomes necessary.

Local exhaust systems should prevent the dispersal of the contaminant and therefore be applied close to its point of origin (grinding, milling, sieving, working with organic solvents).

Operations involving the evolution of irritant or toxic gases should always be carried out in a properly functioning fume cupboard (e.g. with hydrogen sulphide, sulphuric acid, Kjeldahl determinations, nitric acid, hydrofluoric acid and mercury). Benches and fume cupboards should not be deeper than 70 cm.

Toxic and harmful dusts (e.g. arsenic, lead) when produced in such quantity that the exhaust air may be harmful to the surrounding country, should be collected by passing the exhaust air through a cloth filter, a cyclone or an electrostatic precipitator. Explosion reliefs should be fitted.

Ventilators and exhaust ducts should be made of a corrosion resisting, non-combustible and non-absorbent material. Condensation of vapours should be avoided. The construction should be such that periodical cleaning is easy, in order to prevent obstruction by solid deposit and the accumulation of combustible or even explosive residues. Sharp bends should be avoided.



**Lighting**—Adequate and uniform lighting should provide general environmental brightness. Where possible daylight should be used.

A combination of windows and roof lights is preferred. Light colours are helpful: they are pleasing to the eye and, when the general lighting is sufficient, enable the worker to see without effort. Strong contrasts and sudden transitions may become a source of strain and accidents.

Indirect or semi-indirect lighting should be arranged where possible, and in large areas fluorescent tubes are used with good result. They combine brightness and low heat production.

Planned colours are helpful in avoiding mistakes and accidents. They can be used for the identification of pipe lines and in drawing the attention to potential hazards. Numerous codes for pipe line colours are in use in the British Isles and at the time of printing an attempt is being made to unify them into one standard code. In the U.S.A. the code summarized in Table 19 is finding increasing application :

Table 19. Colour Code

<i>Colour</i>	<i>Application</i>
<i>Red</i>	<i>Fire protection equipment</i>
<i>Yellow</i>	<i>Caution</i>
<i>Green</i>	<i>Safety exit, first aid</i>
<i>White and black</i>	<i>Traffic</i>
<i>Blue</i>	<i>Shut down for repair</i>

**Fire prevention**—Correct layout of buildings, including fire walls and fire doors to prevent the spread of fire, proper fire escapes and the use of fire resisting construction and materials where necessary are basic fire precaution measures.

The general principles of minimizing fire hazards are discussed in detail in previous chapters (p 13). For convenience they are summarized below.

Combustible materials should be stored in a separate building located at a proper distance from the main building and provided with an automatic sprinkler installation.

Stocks of combustible solvents in the laboratories should be strictly limited and properly stored. Electric wiring and equipment and the heating system should be safe and properly controlled.

Tidiness and cleanliness are of primary importance and the disposal of waste should be under proper control.

Fire extinguishers, preferably cylinders with carbon dioxide under high pressure, should be amply distributed throughout the

laboratories. They should be kept in working order all the time and regularly checked. Laboratory personnel should be trained in making proper use of them.

In addition to these measures adequate fire fighting equipment should be installed and a sufficient number of employees trained in fire-extinguishing methods. The equipment should be well maintained and regularly inspected and a suitable alarm system should be installed.

In Great Britain there is a statutory requirement under sections 34-37 of the Factories Act 1937 to provide adequate means of escape in case of fire. The responsibility for certification rests with the local council. Additionally, in buildings not being 'factories' as defined by the above Act, local councils can require adequate means of escape to be provided (Section 60 of the Public Health Act 1936). Many of these bodies have their own codes of by-laws for this purpose.

**Storage and transport of glassware and chemicals**—Special care should be taken in the storage and transport of glassware and chemicals.

Chemicals which can react with each other should not be stored in the same place (acids and alkalis ; oxidants and oxidizable material ; sodium and phosphorus).

**High pressure technique**—Cylinders of compressed gases should be stored in a safe place and protected from heat and direct sunlight.

Autoclaves should be operated in a special room or building designed for the purpose.

## INDIVIDUAL PROTECTIVE DEVICES

For emergencies and hazardous work a great variety of individual protective devices are available such as goggles, screens, shields, special clothing and respirators. They should afford reasonable safeguard without being cumbersome. The existence of such devices should not deter attempts to eliminate hazardous working conditions as far as possible by dealing with the hazards at the source.

**Goggles**—Accidents causing temporary or permanent injury to the eyes far exceed all others.

In nearly every instance the victim did not wear goggles through carelessness or through the unjustifiable belief that accidents always happen to the other fellow.

Splashing liquids, flying particles and dust may seriously injure the eyes, but it is always possible to safeguard against this by wearing goggles, a face shield or an acid-hood. Examples of hazardous operations are handling irritating gases, decanting concentrated



acids, alkalis, ammonia, liquid air; preparing solutions, grinding, stamping and sieving, distillation, or combustion in a gas analysis apparatus. Such apparatus may be protected by a screen of metal gauze, splinterproof glass or plastic; goggles or a face shield should be worn during the operations.

It is vital to protect and spare the eyes. In work which requires the wearing of goggles, those which mechanically and optically suit the purpose should be chosen; the nature of the particular work and the hazards determining the specifications.

Spectacle goggles are recommended when instrument readings should be taken; cup-goggles protect the eye against particles flying from the side; rubber mask type goggles protect against splashes of corrosive chemicals and dust. To protect against harmful rays several shades of glasses are available, the spectral absorption properties of which have been standardized in some countries (Tables 48, 49, pp 232, 233).

Goggles should give full protection against the hazards they are intended to protect against. They should be fire and corrosion-proof, strong, light in weight and adjustable. The lenses should be made of laminated glass or plastic, resistant to impact and abrasion. They should provide a wide angle of vision, transmit sufficient light, be non-rusting and easily interchangeable. The different parts of a safety goggle should be interchangeable, capable of being sterilized and should not irritate the skin.

**Safety clothing**—Clothes soaked with a solvent are imminently hazardous because they will accelerate the irritating effect of the substance on and the absorption of the poison by the skin. Moreover clothing impregnated with oils, solvents or certain chemicals constitute a definite fire hazard.

Specific hazards, such as the handling of corrosive chemicals (acids, alkalis), require special clothing. This should give adequate protection combined with comfort and freedom of movement.

Asbestos clothing is available for protection against heat and flame, and leather and rubber for mechanical protection. Rubber, synthetic rubber, plastic and coated fabrics protect against liquids, fumes and dusts.

To protect the hands neoprene and polyvinyl chloride coated gloves have been recommended.

## RESPIRATORY PROTECTIVE DEVICES

Fundamental protection against respiratory poisons and irritants of the air passages should be ensured by proper design of the laboratory and apparatus and careful planning of the work. The escape of any dangerous or irritant gas, solvent or dust into the



## RESPIRATORY PROTECTIVE DEVICES

laboratory atmosphere should be prevented as far as possible by using closed apparatus and closed containers, proper ventilation, the use of a hood, or by working in the open.

Even when all precautionary measures have been taken there will always be operations or emergencies where toxic or corrosive gases, fumes, mists or dusts escape into the laboratory atmosphere. In such cases individual protective respiratory devices must be relied upon.



Figure 20. Self-contained breathing apparatus.

As health and even life may be at stake it is essential to be certain that the protective device is reliable. This implies correct choice of respirator, regular inspection of the protective devices and adequate training.

The ideal protection is given by a self-contained breathing apparatus. This will give protection in any atmosphere.

In emergency cases a gas mask combined with a canister containing a suitable material which retains the contaminant quantitatively can be used. Such a canister gas mask, however, only gives protection if several conditions have been fulfilled : the atmosphere must contain enough oxygen for breathing, the face piece of the gasmask must fit so that no contaminated air can leak in, the canister must contain the proper absorbent and must not leak, and the concentration of the contaminant must be low. Thus it will be obvious that a canister gas mask can only be safely applied in special cases and not for general protection.

In an atmosphere which is irritating to the skin the breathing equipment must be supplemented by a complete suit of impermeable clothing. A self-contained breathing apparatus is illustrated in Figure 20.

### APPARATUS PROVIDING INDEPENDENT AIR OR OXYGEN SUPPLY

The most reliable protection against atmospheric contaminants is given by a respiratory device which ensures an independent source of air or oxygen.

The air-line respirator gives protection against all types of atmospheric contaminants for any length of time. It consists of a hood connected by a pipe to a suitable compressor which supplies pure air slightly in excess of atmospheric pressure. The air supplied must be clean and of a suitable temperature and humidity.

In places where no air-line is available a hose mask may be used, consisting of a face piece connected by a hose line with a hand operated blower situated outside the contaminated atmosphere. Hose masks without blower should not be used, especially in dangerous atmospheres.

Self-contained air or oxygen-supplying equipment consists of a cylinder with air or oxygen, a reducing valve and face piece or face mask. The oxygen breathing apparatus is self-contained and is worn by the user. It is available in sizes providing from one half to two hours supply and is used for rescue work and emergency repair. It consists of a face piece which isolates the wearer from the surrounding atmosphere, a cylinder of compressed oxygen, a pressure regulator, a breathing bag and a canister filled with an absorbent to absorb the carbon dioxide expired by the wearer. The apparatus is complicated and heavy ; it requires considerable training and experience in wearing and maintenance.

The apparatus works on a closed circuit principle. Oxygen is breathed from the bag, the carbon dioxide and excess of oxygen which

## APPARATUS PROVIDING INDEPENDENT AIR OR OXYGEN SUPPLY

are exhaled pass through the carbon dioxide absorbent ; the excess oxygen returns to the bag. The bag is automatically filled from the cylinder through the reducing valve.

The oxygen in the cylinder normally contains a slight amount of inert gas (nitrogen or hydrogen). When the apparatus is in actual service the oxygen is consumed, so that the concentration of the inert gas in the breathing bag gradually rises. As soon as it reaches the threshold value where the partial pressure of the oxygen falls below 120 mm the apparatus no longer gives protection, due to oxygen deficiency. This can be illustrated by the following calculation.

Suppose the circuit has a volume of 11 litre and the cylinder can supply 300 litre of oxygen at atmospheric pressure. We start with the circuit, filled with normal air, containing 79 per cent nitrogen. The threshold value is reached when the circuit contains 85 per cent nitrogen *i.e.* when  $(0.85 - 0.79) \times 11 = 0.66$  litres of nitrogen have been supplied by the oxygen cylinder. The oxygen therefore should not contain more than this volume of nitrogen *i.e.*  $0.66 : 3 = 0.22$  per cent.

Consequently it is essential to use oxygen of high purity and to start with freeing the circuit from atmospheric air by inhaling, squeezing the tubes and exhaling so that atmospheric air escapes past the rim of the face piece.

There is also a self-contained apparatus utilizing potassium peroxide which by reacting with the moisture in the exhaled breath produces oxygen, at the same time absorbing the carbon dioxide.

## GAS MASKS

In emergencies, provided that the surrounding atmosphere contains sufficient oxygen, protection is afforded against noxious or troublesome dusts and vapours, toxic fumes or gases, by a gas mask which isolates the respiratory organs from the surrounding atmosphere. The mask is connected with a canister, which absorbs the contaminant during a limited time and for relatively low concentrations of the toxic substance.

The gas mask must isolate the wearer from the surrounding atmosphere. This should be checked by the wearer before entering the contaminated atmosphere. Gas masks are available in various sizes ; every user should know his size. A good mask is provided with inhalation and exhalation valves which considerably reduce the breathing resistance.



The canister is usually screwed on to the gas mask. Masks with large and heavy canisters are provided with rubber tubing connecting the face piece with the canister, which is worn in a harness.

The face piece should be flexible, close fitting and attached by adjustable elastic harness. The mask is provided with eyepieces of non-splintering glass. The inner surface of the eyepieces should be covered with a thin layer of anti-misting material.

The actual canister of a canister mask is intended to remove small amounts of contaminating vapours from the air which is drawn through it. It must not be used where there is likely to be a deficiency of oxygen, where the proportion of contaminant is high (over 1 per cent) or for any length of time.

The canister must have the right absorbent for use against the particular vapour which is to be removed, see Table 45, p 226. The packing must be very even so as to avoid any channelling and the resistance to breathing must be as low as is consistent with proper removal of the contaminant.

The toxic constituents of the inhaled air may be removed in four ways :

- a* mechanical filtration
- b* absorption by substances with a large active surface
- c* absorption by chemicals, mostly applied on a porous carrier
- d* catalytic conversion to a harmless substance.

The first principle is applied to arrest fine dust, smoke and haze.

The most usual physical adsorbent is active carbon, it is suitable for the removal of vapours of organic solvents. The degree of adsorption of various gases depends upon their boiling point and critical temperature. Gases with a high boiling point are adsorbed preferentially. An adsorbed gas may be displaced by another less volatile gas.

Chemical absorption is resorted to for chemically active gases, which on account of their low molecular weight are not sufficiently retained by active carbon : hydrogen cyanide, ammonia, hydrogen sulphide, halogen acids, sulphur dioxide, nitric oxide and nitrogen peroxide.

For acid gases (halogens, halogen acids, hydrogen sulphide, hydrogen cyanide, sulphur dioxide and nitrogen oxides) a charge of alkali hydroxide on a porous carrier (pumice, silica gel or active carbon) is applied.

For the absorption of ammonia a carrier (pumice, active carbon) is impregnated with phosphoric acid, cuprous sulphate or zinc chloride.

## APPARATUS PROVIDING INDEPENDENT AIR OR OXYGEN SUPPLY

Carbon monoxide forms a problem apart. It is neither absorbed by active carbon nor absorbed by chemical reagents. There exists only one method to eliminate it : oxidation to carbon dioxide, which is harmless in small concentrations. In order to achieve this oxidation at room temperature the contaminated air is led over a catalyst of hopcalite. This catalyst is rendered inactive by moisture, and it is therefore protected in the canister on both sides by a layer of calcium chloride or silica gel. In some types of canister a layer of calcium carbide is provided to warn the wearer by the smell of acetylene when the drying agent has become inactive. As soon as the smell of acetylene becomes perceptible, the catalyst and the drying agent must be renewed.

A combination of different fillings yields a canister for general use. The single type of canister, however, has a longer life and is more economical.

As a rule the nature of the gas against which protection is required is known. If this is so, the corresponding canister should be used. The canisters are distinguished by a conspicuous colour (Tables 42-44, pp 223-26). Unfortunately these colours have not been standardized internationally up till now.

As the gas penetrates into the layer of absorbing material its concentration decreases gradually. As soon as the absorbent is saturated the canister must be changed for a new one. Sometimes the smell provides a warning that the absorbent needs changing, but the smell is subjective and consequently not a reliable guide. The periods of actual service of the canister must be recorded on a card, inspection of which will show when the canister must be discarded or regenerated. If the mask is used in emergencies only it is safest to replace the canister each time it has been used.

**Control and Maintenance**—In order to test the canister its absorbing capacity should be determined. A mixture of air and contaminant is passed through at a given rate for a definite time and the unabsorbed contaminant is determined as a function of the amount of contaminated air that has passed through the canister. It is also necessary to inspect regularly all mechanical parts of the mask including the operation of the valves as well as the resistance to breathing developed by the canister.

All parts of the apparatus, except the canister, should be cleaned after each use *e.g.* by washing with soap and water, and sterilized *e.g.* with formaldehyde, before being passed from one employee to another.

The masks and canisters should always be ready for use and preferably be stored in a cool room, away from direct sunlight to protect the rubber. The canister should be protected against moisture.



Efficient use of the gas mask requires repeated training in putting on, adjusting, wearing and working with the gas mask. This training also enables selection of persons fit for this kind of work to be made.

**Dust masks**—These masks give protection against dust by mechanical filtration. The major characteristics of a filter respirator are the size of the particles retained, the completeness with which the dust is removed and the resistance to breathing.

There are many types of dust masks available but the basic principle of operation is the same in all. A layer of porous material is interposed between the nose and mouth of the wearer and the dust-laden air. Air is drawn through this pad and is filtered in the process. The life of these masks is relatively short as the pores become clogged with dust and ultimately breathing becomes too restricted to enable the mask to be used. It is an advantage to allow wearers to select the type of dust mask which they find most comfortable. If this is done, there is less likelihood that they will avoid wearing it.

### FIRST AID

It is always best to call a doctor. The following recommendations are restricted to general measures in giving first aid to casualties. It is well to remember that all patients who have been burned at all severely, who have taken poisonous substances internally, or lost much blood suffer from some degree of shock. This is more important than the local condition and should be treated first.

**Treatment of shock**—The patient feels faint, complains of thirst and may vomit. The face is pale and the skin cold and clammy, the pulse is rapid and breathing is weak. Even if these symptoms are absent the presence of shock should be assumed and appropriate treatment given.

The patient should be made to lie flat, with the feet raised and the clothing loosened at the neck, and wrapped in blankets and kept quiet. Plenty of fluids, such as warm sweet tea, water or weak saline should be given. Alcohol is to be avoided. Liquids should never be forced between the lips of an unconscious patient. Artificial respiration or oxygen may be administered if breathing is feeble or has ceased.

**Haemorrhage**—Venous or arterial bleeding must be stopped by applying pressure to the wound, or using a tourniquet. Treatment for shock should be given.

**Cuts and wounds**—A mixture of hydrogen peroxide and warm water is used to clean the wound and surrounding skin, which is then painted with acriflavine or iodine and covered with a dry dressing.



**Corrosive substances**—Strong acids, alkalis and phenols damage the skin and the eyes. They should be removed by flushing immediately with plenty of water. Substances insoluble in water, such as tar and naphthalene, may be removed with a neutral oil *e.g.* toilet paraffin.

When corrosives have been swallowed it is best to give activated charcoal followed by an emetic. When drops of corrosive liquids splash the face, the eyes must be kept closed until the drops are washed away with plenty of water. Everyone should know where taps, showers, eyebaths and douches are placed.

The most commonly used chemicals which may attack the skin and the mucous membranes are given in Table 39, p 216.

**Clothing on fire**—If clothes catch alight, the flames should be extinguished by douching with water or by applying the carbon dioxide fire extinguisher. To prevent the flames from reaching the head of the victim he is laid flat on the floor. The burning clothes can then be extinguished by covering the victim with a fire blanket which should be pressed firmly to the body over its whole length or by rolling the patient to and fro in the blanket, pressing the body on to the floor to extinguish the burning clothing.

**Burns**—Burns may be caused by flames, by electricity, by hot and by very cold substances such as liquefied gases, by corrosive chemicals and by friction. They are sub-divided into three degrees:

- a* burns of the first degree result in a swelling of the skin, which is red and painful
- b* burns of the second degree form blisters
- c* burns of the third degree are characterized by necrosis—the skin appearing brown or black, sometimes white.

Often it is necessary to inspect the burned part of the skin and its environment. Clothing must never be pulled off a burn, it must be cut off with a pair of scissors, leaving in place all parts which stick to the skin. The area should be covered with a bandage. Violent removal of adhering material might open wounds which may easily become septic. In burns of the third degree, clothing usually sticks to the burned skin.

**Treatment of first degree burns**—These burns are treated by the cold water cure. Especially when burns are caused by corrosive fluids, such as acids and alkalis, flushing with water for a long time is essential. The burned member should be immersed in cold fresh water, which is continually renewed, until all sensations of burning and pain cease.

**Treatment of second degree burns**—If a burn results in the formation of blisters first aid should consist in applying a dry sterile dressing. Cartons or tins of these dressings ready for use should be kept at

hand. The blisters should not be burst open, nor should the dressing be applied tightly. Its purpose is to prevent the blister from opening or, should it burst, to ensure that it will do so in sterile surroundings.

**Treatment of burns in the third degree**—Such burns are treated only by applying a dry sterile dressing. The purpose is to prevent the burnt piece of the skin from being rubbed off and the burnt area being injured. This would produce an open wound with danger of subsequent infection. The dressing should therefore be applied over any pieces of clothing adhering to the burn. Third degree burns need proper medical treatment as soon as possible.

The degree of burning is of far less importance than the total area of the burn. When a large area of the body surface is burned, complications such as shock and infection may arise which are more serious than the burn itself. Local treatment may therefore be less important than general treatment, especially in mitigating the effects of shock. The patient should be kept warm during the time he is waiting for the doctor and during the journey home or to the hospital.

Burns are very serious if more than one third of the surface of the human body is affected, even if the burns are only of the first degree. Hospital treatment is essential. Such a patient should not be moved unless qualified medical aid is not available for a considerable time. While waiting for the doctor the patient must be kept warm with blankets and hot water bottles. The latter should always be covered with a blanket or a wollen sock to avoid burning the patient: shock cases burn easily. Applying other than dry sterile dressings is only a hindrance for a quick and efficient treatment in hospital.

In treating cases of burns a complication may arise due to poisoning arising from the products of combustion of the chemical which has been burnt. This is particularly apparent in the case of nitro compounds, such as some explosives. The products of combustion usually contain nitric acid which may poison the wound and slow down recovery.

**Inhalation of poisonous fumes or gas**—The patient must be removed from the poisonous atmosphere, kept warm and quiet and given artificial respiration or oxygen if necessary.

**Carbon monoxide poisoning**—An oxygen breathing apparatus or suitable respirator should be worn by rescuers entering an atmosphere containing carbon monoxide. The respirator is to be used only if there is no doubt that the oxygen content of the room is sufficient to satisfy physiological requirements during the work of rescue and provided the carbon monoxide concentration is less than 2 per cent.

The patient is brought into fresh air. In severe cases, headache,



# FIRST AID

Table 20. Antidotes of Poisons

Poison	Symptom	Antidote
<b>Corrosive poisons :</b> Strong acids (sulphuric, hydrochloric, nitric), also strong alkalis, such as caustic soda, lime, and potash	Burn and stain on the lips and mouth, burning pain in throat and stomach, straining and vomiting, perhaps suffocation, shock always present	For acids : give baking soda, magnesia, lime water or soap suds. For alkalis : give vinegar, lemon juice. Also, for both poisons give large doses of olive oil, milk, eggs, or flour and water, to dilute and soothe the parts, then induce vomiting
<b>Irritant poisons :</b> Mercury, lead, antimony salts, arsenic, phosphorus, poisonous plants, cyanides	These do not stain. Metallic taste in mouth, burning in throat and stomach, vomiting and purging	Dilute and soothe with large quantities of salad oil, milk, eggs, soap suds, starch, or flour water, then induce vomiting with salt water or mustard and water. Follow by stimulants like strong coffee or tea, or spirits of ammonia (no oil for phosphorus poisoning)
<b>Nerve poisons :</b> Opium, morphine, paregoric etc	Produce deep sleep, pupils of eyes small ; insensibility ; face flushed	Induce vomiting if poison is just taken. Keep awake by strong coffee : slapping with wet towels : walking the victim supported on each side, and artificial respiration
Strychnine, belladonna, hydrocyanic acid etc	Convulsions, twitching, delirium, and suffocation	Induce vomiting at once, apply artificial respiration if breathing stops ; give stimulants
Iodine	Staining, burning etc	Two tablespoons of starch in a teacup of water, either corn starch or laundry starch ; produce vomiting
Phenol	Vomiting and great pain ; skin covered with cold sweat. Very rapid poison ; lips, tongue and mouth are burned white by pure, and black by impure, phenol	A couple of tablespoons of either Epsom or Glauber salts in water. Lime water is not so effective. Three or four raw eggs or castor oil. Give stimulant
Silver nitrate		Salt and water



cramp, nausea and vomiting may be present. The face is red. Oxygen or artificial respiration should be administered, keeping the patient warm and quiet. Patients suffering from carbon monoxide poisoning are liable to be aggressive and may refuse treatment, but first aid must be given firmly. Medical aid should always be summoned.

**Aniline poisoning**—In acute aniline poisoning characterized by cyanosis and quick superficial respiration oxygen should be administered. Artificial respiration is liable to make the patient's condition worse. In chronic aniline poisoning, rest and change of work should be prescribed.

**Oral poisoning**—Dilution is much more important than the administration of an antidote. Quantities of water or tea should be given. Poisons such as alkaloids may be adsorbed by activated charcoal : 10 gm in 100 cc.

The poison is eliminated by giving a simple emetic (soapy water, or mustard and water). Washing out the stomach should be carried out only by a doctor.

It is dangerous to induce vomiting when the patient has swallowed corrosive acids, alkalis or salts. It is best to give diluting and at the same time neutralizing drinks (magnesia, lime water, milk, 0.2 per cent ammonia solution, or lemon juice) and leave the rest to the doctor. Carbonates or bicarbonates should not be given for acid poisoning.

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## SAFETY INSTRUCTIONS AND REGULATIONS

### GENERAL ORGANIZATION

**A**LL PERSONNEL, including the maintenance men, must know the safety regulations and act accordingly. An adequate supply of safety appliances should be provided, such as sand boxes, fire extinguishers, fire blankets, showers, goggles, shields, protective clothing and respirators. All personnel should know where to find the safety devices and be instructed and trained periodically in handling them.

All laboratory workers should be trained in the principles of glassblowing and the handling of poisonous, inflammable and explosive materials.

Orders for operations outside the scope of routine work should be given in writing. The dangers connected with the work and the precautionary measures should be stated in this order. Preliminary tests with dangerous and explosive materials should only be executed after the advice of the departmental head has been taken. The results should be entered in a book intended for the purpose.

At the end of working hours all gas taps and electric heating apparatus should be switched off. All connected gas tubes and sinks should be checked and waste containers emptied.

Everybody should know who is qualified to render first aid in case of accidents. All accidents and dangerous occurrences should be reported at once. Carrying out unauthorized experiments should be strictly forbidden.

In the case of a serious accident, a report should be made which gives the circumstances. The purpose of this report should be not to fix blame but to decide on measures to prevent a recurrence. Statements of witnesses should be taken and every effort made to make the report as complete as possible. The report should also make recommendations for preventing a recurrence. It is often convenient to have forms printed for making these reports. The design of such a form requires careful consideration because, once instituted, it should not be altered unless absolutely necessary.



## GENERAL SAFETY INSTRUCTIONS

### GENERAL SAFETY INSTRUCTIONS

Turn off gas taps when burners are not being used.

Keep burners, tubing, valves and apparatus in perfect condition. Inspect the rubber tubes regularly ; protect them from contact with chemicals and do not expose them to heat.

See that electrical apparatus is set up safely and is properly earthed. Use only undamaged, well insulated wires.

Before using portable electrical apparatus check for worn or defective insulation, loose or broken connections, and see that the earth wire is connected. Keep leads as short as possible. Avoid trailing wires ; coil excess wire neatly. Keep electrical cables away from a hot surface. See that no water can leak on to electrical plugs and switches. All permanent wiring should be installed by a qualified electrician.

When liquid has been spilled on a motor, the latter should be stopped, the current switched off and the motor dried. Newly bought electrical apparatus should be inspected by an electrician before it is allowed to enter the laboratory.

Do not allow bottles and apparatus to accumulate at the back of benches. Keep excess apparatus in the stores, not in the laboratory room. Do not leave pipettes lying about on the bench, put them in the rack, properly rinsed, immediately after use.

Wear rubber gloves when handling caustic chemicals. Make sure that they are not porous or defective. Rubber gloves, or any other type of glove which is impervious to the liquid being handled, are only safe so long as they are free from holes. They should always be long enough to ensure that liquids do not get inside the gloves. If they are not fabric lined, care should be taken to wash the insides as well as the outsides after use. When not in use they should be kept on special hooks, fingers uppermost so that they may drain readily after washing.

Do not drink from beakers. Do not use tableware for chemicals. Take your meals outside the laboratory *e.g.* in the canteen or in the open air. Wash your hands when they have been in contact with chemicals. Never use organic solvents for this purpose but a good soap. Always use your own wash bottle. This is hygienic and moreover the contents of other wash bottles are not known.

Do not allow inflammable, poisonous and corrosive gases to enter the vacuum line. Acid gases and ammonia can be retained by means of a washing bottle containing an absorbing liquid.

If water or chemicals are spilled on the floor, laboratory table or instruments, have them cleaned up or removed immediately. Some chemicals should first be neutralized or diluted. Laboratory benches and floors should be cleaned regularly. Waste containers

## SAFETY INSTRUCTIONS AND REGULATIONS

should be provided for the disposal of broken glassware ; metal containers with self-closing covers for oily rags and for inflammable liquids. They should be emptied daily.

Report any accident and have each injury attended to immediately.

### HANDLING GLASSWARE

Inspect all glassware before using it. Do not set broken or damaged glass apparatus aside but take it to the glassblowers' shop, where it should be repaired as soon as possible.

Deposit broken or unmendable glassware in the container intended for the purpose.

Only use glass tubing the ends of which have been flame-polished to remove sharp edges. When connecting glass tubes with rubber, the tubing ends should be lubricated and then inserted into the rubber connecting tube until the ends butt together.

Never force glass tubes or a thermometer through a cork or bung. The hole should be of the proper size and the cork borer, glass tube or thermometer which has to be inserted in the stopper should be lubricated with glycerol, or inert grease.

When boring a stopper do not hold your hand over the stopper on the side opposite the borer. Hold the stopper between thumb and finger and rest it against a wooden block.

Use heat resistant glassware exclusively for dissolving and diluting chemicals, and porcelain containers for mixing chemicals.

Use a substantial support *e.g.* a tripod, when handling big flasks.

When working with an ice mill keep your hands out. If glass gets into the ice, the whole should be discarded.

While pipetting keep the point of the pipette well below the level of the liquid. Take care that the liquid does not get into your mouth.

When pipetting caustic, volatile or irritant liquids, use a suction pump. Clean the pipette after use. Do not pipette harmful liquids. Use a burette or a measuring cylinder instead. Do not pick up glassware that may be hot. Use tongs or asbestos fingers when handling hot objects.

### STORAGE AND TRANSPORT OF CHEMICALS

Access to stores, dispensing and transportation of chemicals should be limited to authorized personnel who should be fully trained and instructed.

Do not store acid and ammonia, oxidizing and reducing agents or other pairs of reacting chemicals near to each other *e.g.* sodium (under paraffin) and white phosphorus (under water).



## CLEANING GLASSWARE

All bottles, tins and casks in which chemicals are kept or transported should bear a label clearly indicating the contents.

Never fill a receptacle with material other than that indicated by the label. Throw away the contents of unlabelled containers.

Poisonous and inflammable chemicals should not be kept on laboratory shelves but in a separate room or cabinet.

Do not put bottles containing caustic chemicals on upper shelves. Open such bottles carefully. Wear goggles.

Replace the stopper and return each bottle to its proper place on the shelf immediately after use. Keep reagent bottles in their correct places on the shelves.

Store heavy containers on or near the floor. Do not store bottles on shelves above or near gas burners. Uncovered containers should be prohibited.

Do not carry a bottle by the neck. When transporting large bottles use the apparatus provided for the purpose.

Be careful when transporting large beakers and jars. Carry them in both hands, make sure that the floor is dry and not slippery ; use gloves.

Do not use a chair or stool when taking a bottle down from a shelf. Use a reliable ladder. Slipping in a laboratory is dangerous.

Do not use a match or unprotected flame to ascertain whether a cask or drum is empty. Use an electric torch.

Carboys and demijohns may break or crack. Use them only when the protecting basket is in good condition. Put the bottle in such a position that it may be emptied safely. Use a syphon. Remove the syphon after use. Bottles containing liquid having an appreciable vapour pressure at room temperature (ether, acetone, alcohol, petrol, benzene, bromine, nitric acid, hydrochloric acid) should never be filled completely, or exposed to sunlight or stored in a warm place. Open such bottles carefully wearing goggles.

Glass tubes should never protrude from the racks.

## CLEANING GLASSWARE

Cleaning glassware and instruments with organic solvents should always take place in a special room intended for the purpose ; this room should be properly ventilated.

Etching and cleaning of glassware by means of hydrofluoric acid should be left to the staff of the glassblowers' shop. The use of goggles and rubber gloves or rubber fingers is obligatory.

Cleaning and filling of hydrogen sulphide generators should be carried out in a special room or in the open air.

An ammoniacal silver solution should not be stored but decomposed after being used, by adding dilute hydrochloric acid in excess.



## SAFETY INSTRUCTIONS AND REGULATIONS

The preliminary cleaning of glassware which has contained caustic materials or material which may be hazardous in use should not be left to inexperienced assistants. The person carrying out the experiment should remove all dangerous chemicals from the used apparatus before discarding it. This is especially important in the case of sodium or potassium metal or certain peroxides, or such chemicals as acetyl chloride, which have a violent reaction with water. Such materials should be dissolved out carefully, using a suitable solvent *e.g.* alcohol for metallic sodium or potassium.

### HANDLING STRONG ACIDS, ALKALIS AND AMMONIA

Learn the operation of the shower, wear protective clothing (leather or rubber apron, rubber boots and gauntlets) and goggles.

Never pour water into acid. Keep acid away from combustible material.

Protect acid bottles against heat and sunlight. Immediately they are empty rinse bottles thoroughly. Keep and transport strong acids exclusively in closed bottles which are protected against breakage by means of a carrier. Keep the outside of acid bottles and the stopper clean and dry. Do not place the stopper on the bench.

Always be on your guard for splashes when opening an acid bottle : wear goggles or a face shield.

Measure strong acids and similar liquids by means of a graduated glass cylinder : never use a pipette.

When corrosive materials have been spilled on laboratory floors, cleaning should be carried out under experienced supervision. It is advisable that instructions should be prepared beforehand so that the steps to be taken are well known by all concerned. The acid or alkali should first be neutralized. Soda ash is better than limestone or hydrated lime for sulphuric or phosphoric acids because of the low solubility of calcium sulphate and calcium phosphate.

Sometimes it is necessary to take precautionary measures against the carbon dioxide formed during neutralization of acids.

If you have spilled acid on any part of the body flush it immediately with water. Do not pour acid into the sink. Ammonia and alkalis should be neutralized with an acid before flushing.

### POISONOUS CHEMICALS

Experiments with poisonous chemicals or operations during which harmful gases may be formed must be performed in the open air or in a fume cupboard. The functioning of the hood should be checked. If in spite of these precautions harmful gases enter the room, provide yourself with an appropriate respiratory device and see that no unprotected persons enter the room.

## ORGANIC SOLVENTS

Clean the apparatus and glassware which have been in contact with the poisonous substance, personally and at once.

Place apparatus containing mercury in a tray or on a specially constructed table so that spilled mercury can be collected readily.

Purify mercury only in a properly ventilated room, preferably in a fume cupboard. The concentration of the nitric acid used for the purification should not exceed 10 per cent.

Distillation of mercury should be carried out under a fume hood. When mercury has been spilled it has to be removed as completely as possible, after which the tailings must be inactivated *e.g.* by means of flowers of sulphur.

When highly toxic gases such as chlorine, carbon monoxide and nitrogen oxides escape in a room this should be vacated immediately. Only persons provided with proper respiratory protective devices, such as a self-contained breathing apparatus, an air-line hose mask or, when there is no doubt whatever that the atmosphere contains sufficient oxygen, a gas mask with the appropriate canister, should be allowed to enter the room.

Windows should be opened and water sprayed. Anyone who may have breathed nitrogen oxides should undergo medical examination.

In removing spilled nitric acid, do not use porous organic materials such as sawdust, but dilute with water and neutralize with calcium or sodium carbonate.

## ORGANIC SOLVENTS

Vapours of organic solvents are inflammable and toxic. Replace carbon sulphide, benzene and chlorinated hydrocarbons by less toxic solvents wherever this is possible. Less toxic solvents are petroleum naphtha, acetone, ether or xylene.

If you are working with a separating funnel containing a volatile solvent, hold it with the cock turned upwards. Open the cock regularly in order to release any pressure set up inside.

Solvent vapours are heavier than air and consequently have a tendency to collect near the floor of the room or to travel along the bench top so that they may be ignited by a distant flame.

When using an inflammable solvent, put out all flames in the neighbourhood and do not smoke. Avoid the generation of static electricity. Do not use spark-producing equipment. Keep a fire extinguisher at hand.

When handling organic solvents regularly, ascertain whether the fume hoods function properly, wear an air-line respirator or in emergencies a gas mask with activated carbon canister if necessary. Keep the apparatus and containers closed and close them again immediately after use. Do not pour solvents into the drains, never



wash your hands in an organic solvent ; do not spend meal times in the laboratory, go into the open air when possible. Take care of your health outside the laboratory also.

If a symptom which might indicate poisoning by organic solvent is noticed consult a doctor.

## HANDLING HIGH PRESSURE APPARATUS

**Autoclaves**—An autoclave must be provided with a properly adjusted safety valve and inspected regularly. The following points should be noted :

- a* contents
- b* pressure and temperature at which the apparatus has been tested
- c* maximum admissible working pressure and temperature
- d* material of which the vessel is made
- e* available volume.

The test pressure must be at least 1.5 times the working pressure. Testing should be repeated periodically. Special attention must be paid to permanent deformations. All data should be recorded.

The apparatus should always be provided with a pressure gauge. The safety valve must be adjusted to a pressure not exceeding two thirds of the test pressure.

In calculating the 'available volume' it is not the best practice to allow a definite proportion of the vessel as 'free space'. The figure given is usually between 10 and 20 per cent. The change in volume due to the reaction and the pressures which will develop as the reaction proceeds should be calculated. This figure will give the pressure likely to develop during the course of the reaction and will also ensure that sufficient space is left.

Autoclaves should be operated only in places intended for the purpose and arranged in such a way that nobody can be injured if something should go wrong with the apparatus. The instruments should be set up behind a steel wall, so that the operator need not go near the autoclave during the experiments.

At the end of each run autoclave, pressure gauge and safety valve must be cleaned and checked.

If little or nothing is known of the behaviour of the substances concerned under the conditions to be expected during the experiment, a small scale experiment should be performed first.

Such preliminary tests should be approved of by the departmental head and the results recorded in a special book.

Before an autoclave is used at a temperature for which it was not originally intended it should be examined as to whether the *properties of the material* at this temperature permit its use.



## HANDLING HIGH PRESSURE APPARATUS

**Glass under pressure**—Glass apparatus used for pressure or vacuum experiments as well as apparatus with liquid air, oxygen and nitrogen should be sufficiently strong. Do not use thin-walled or flat bottomed flasks for this purpose. Protect such apparatus *e.g.* suction flask, vacuum desiccator and vacuum distillation apparatus, with a mantle of wire gauze or a shield of safety glass.

Always wear goggles when operating such apparatus.

Make certain that the rubber stopper or filter crucible of apparatus which is being evacuated (desiccator, suction flask, distillation flask) cannot be sucked into the neck of the flask.

Before the flask is disconnected or opened it should have cooled down to room temperature and air must be admitted carefully.

During heating and subsequent cooling of liquid filled glass tubes *e.g.* Carius tubes, these should be surrounded by a metal tube : when being opened they should be wrapped in a cloth. Use a safety shield and wear goggles.

**Gas cylinders**—Cylinders containing compressed gases should be distinguished clearly, preferably by a coloured band and the name of the gas. The corresponding pressure regulator should be painted the same colour. Cylinders should be handled with care and stored in a cool place. The metal cap should be kept in place when the cylinder is not in use. Never force connections that do not fit.

Cylinders with poisonous gases should be stored and, if possible, used only outside the laboratory, and checked for the absence of leaks by means of a soap solution.

Cylinders should be used in an upright position and fastened to the wall or the bench by an adjustable chain to prevent accidental tipping. The base should rest on a stand.

Before connecting a cylinder with the pressure regulator the valve is opened for a moment to remove dust or dirt. Do not use a cylinder without the corresponding pressure regulator. Do not permit the gas to enter the regulator suddenly. This is the main cause of explosions in the pressure regulator of an oxygen cylinder, the heat of compression igniting the hard rubber packing inside the regulator. There are special valves to prevent the pressure in the regulator from setting up too suddenly.

Before removing the regulator from the cylinder, close the cylinder valve and release all gas from the regulator. Pressure regulators should be checked regularly.

**Oxygen cylinders**—These should not be stored in the vicinity of combustible material.

Keep the valve of an oxygen cylinder free from oil or grease. Never fill an oxygen cylinder with another gas, nor other cylinders with oxygen. Never substitute oxygen for compressed air.

**Acetylene cylinders**—Cylinders containing acetylene should be used in an upright position. Keep the valves free from oil and grease.

Special attention should be paid to leaks. If the cylinder has caught fire or gets hot, extinguish the flame, close the valve, cool the cylinder with water and remove it to a safe place in the open. A cylinder which keeps hot is dangerous, the heat development indicating spontaneous decomposition of the acetylene. The decomposition is exothermic and may become explosive.

When the pressure in the acetylene cylinders has reduced to 2 atm they must be refilled, otherwise they lose too much of the acetone which serves as a solvent for the acetylene, thereby reducing the risk of explosion.

**Hydrogen cylinder**—When a hydrogen cylinder or a cylinder containing any other combustible gas catches fire, extinguish the flame, close the cylinder and cool it.

In dealing with cylinders containing liquefied gases (acetylene, ethylene, ammonia, sulphur dioxide, carbon dioxide) it is very convenient to control the emptying of the cylinder by keeping it permanently on a balance; provided the tare of the cylinder is known and the weights carefully recorded, a very easy check can be kept on the amount of gas remaining in the cylinder. It will be found advantageous to stamp the tare of any cylinder on it.

When a cylinder with chlorine is leaking keep to the windward side and warn all persons in the path of the vapour cloud. Spray freely with water, or immerse the cylinder in a trough.

When connecting a cylinder with an apparatus, a safety valve should be provided for in case the passage of the gas should become blocked.

After the work has been ended or at the end of the work day, the apparatus should be disconnected.

## **HANDLING INFLAMMABLE AND EXPLOSIVE CHEMICALS**

Inflammable and explosive chemicals should be stored in a fire-proof place outside the main building. This store room should be provided with an automatic extinguishing system.

In the laboratory proper, inflammable liquids should only be present in bottles not containing more than one litre each, or else in metal containers. They should be handled only in the absence of open flames. Special care should be taken with liquids of low flashpoint such as carbon disulphide, ether, acetone.

Do not use a free flame in a distillation of inflammable liquids. Use a steam bath, a water bath with immersed electric heater, an enclosed hot plate or an electric heater surrounded by a suitable insulating material.



The distillation flask should never be filled for more than one third and should always be refilled at room temperature. Fresh pumice should be added to the liquid before heating. Do not heat too rapidly and avoid local overheating. Place a safety glass shield before the apparatus, wear goggles and keep a fire extinguisher near at hand.

When large quantities of inflammable liquids have to be treated (more than 1 litre) the operations should be performed in a separate room, not directly connected by an open door or passage with the main building.

Do not pour waste inflammable liquids into the sink. This might give rise to explosions in the sewer line. Deposit wastes in metal containers provided with a suitable lid. They should be emptied daily.

There is a statutory requirement in Great Britain under the Petroleum Consolidation Act 1926 : liquids which give off an inflammable vapour are not allowed to go into local sewers, which means that steps must be taken by the provision of a settling tank or a labyrinth to ensure that the solvent is retained. Any such separator should be designed to allow vapours arising from the solvent to escape into a safe place.

Do not throw a lighted or glowing match into a waste container.

Place a phosphorus pipette in a metal container so that if the glass pipette should break the water cannot leak away, leaving the phosphor dry and in contact with the air.

When phosphorus pipettes are being filled or cleaned they must be kept immersed in water to prevent the phosphor coming in contact with the air. Do not touch the phosphor with the fingers : use tongs.

If the phosphor must be dried between filter paper *e.g.* for making a solution of phosphor in carbon disulphide, this should be performed under a big converted funnel while a stream of carbon dioxide is supplied through the funnel.

An apparatus containing an inflammable or explosive gas should be cleaned directly after the experiment (if hot, after cooling) by the operator either by filling it with water or by passing air through it.

Gasmeters and flowmeters should be flushed with nitrogen before use. When experimenting with explosive gases, make use of tightly fitting rolls of copper gauze as flame arresters in appropriate places.

Flush glass apparatus with air before having it manipulated by the glass blower.

Experiments with an explosive substance should only be carried out in the open air or in a space designed for this purpose and even

then only by special order and after a preliminary test has been made. The results should be recorded in a special book.

**Ether**—A considerable number of organic chemicals, of which ether is probably the best known, can form peroxides. These are usually liquids having a formula similar to that of ether. The formation of peroxide can be inhibited by the use of a number of chemicals but it should be borne in mind that these inhibitors will only prevent the formation of peroxide but will not destroy any peroxide which is already present. Such solvents should be stored in bottles covered with black paper and in a dark cupboard. The average laboratory brown glass bottle will not prevent formation of ether peroxides. Any ether in store should be tested regularly for peroxide and if it is present it should be removed by means of acid ferrous sulphate solution.

**Inflammable wastes**—Thimbles, filters, cotton wool and similar materials impregnated with inflammable liquid should not be deposited in the normal waste containers, but burnt in the open air. Store perchloric acid away from all inflammable materials including wooden shelves and floors. Surround the container with enough inert inorganic absorbent material to absorb the acid if the container should break or leak.

Use gloves and goggles when handling perchloric acid. Thoroughly clean all apparatus which has been in contact with the acid. Carry out evaporations in a special hood of non-flammable construction. The exhaust system should be regularly inspected and cleaned.

Oxidize organic matter completely with nitric acid before adding perchloric acid. Dilute residues before disposal.

Mixtures of perchloric acid and an organic substance are potentially powerful explosives.

**Sodium**—When drying ether or alcohol with sodium, take care that no water can accidentally enter the reaction vessel. Do not heat an apparatus containing sodium on the water bath or a steam bath. Use an oil bath or an electrically heated jacket. Pass a current of nitrogen through the apparatus during the experiments.

**Pyrophoric material**—Store pyrophoric powders in closed containers. When transferring such a powder take care that none of it is spilled. Clean up any spills immediately and flush with water.

**Chromic acid**—Use stainless steel vessels or glass vessels protected by a stainless steel jacket to store solutions of chromic acid. Cover the container with a stainless steel lid. Fasten cylindrical containers to prevent them being knocked over.

**Liquid air etc**—Do not pour liquid air, oxygen or nitrogen. Use a syphon. Keep the containers covered when not in use.



## FIRE FIGHTING

**General precautions**—Do not leave gas burning. Switch off electrical heating apparatus overnight.

Examine all gas tubing before and during use.

Never throw butts of cigarettes or cigars into the waste containers, on the floor, in the corridors or out of the window. General prohibition of smoking is the only alternative.

Do not place heating apparatus near walls. Insulate it from the bench by sheets of asbestos, preferably with an air space between the table and the asbestos, never with inflammable materials.

Do not leave liquid-filled wash bottles and similar flasks on the bench exposed to direct sunlight.

For fire fighting every laboratory room should be provided with buckets filled with sand or earth, carbon dioxide extinguishers, blankets, and showers at or near the entrance and exit. All personnel should know the location of these and be trained in handling them. They should be checked regularly. In case of fire act immediately, preferably using carbon dioxide or sand.

A liquid burning in an open container should be shut off from the air by covering the container. Never use water in such a case.

Do not sprinkle sand on moving parts of apparatus. After using a fire extinguisher, be sure that the fire is out and that the extinguisher is made ready for use again.

If clothing catches fire, the victim should be placed on the floor so that the flames cannot reach the head. Try to extinguish the flames by means of a blanket. The carbon dioxide extinguisher may also be used for the purpose, but there is danger of suffocation by the carbon dioxide.

**General measures in case of fire**—If in spite of direct action a fire develops into a blaze the room must be evacuated and the fire brigade summoned. Turn off the gas and switch off the electric current. Keep the doors of the rooms and any doors in the corridors closed. If the room is provided with air conditioning this must be switched off.

Whenever possible any inflammable chemicals in the vicinity of a fire should be removed, but it should be remembered that work of this sort should not be done by young and inexperienced staff as it is almost certain that at some time a decision will have to be taken as to whether to leave these materials to burn or to risk one's own life. If removal is impracticable a stream of water should be played over them, especially with cylinders containing inflammable gases. Should cylinders containing nitrogen and carbon dioxide be available, there is no reason why, before leaving the room, these should not be opened in an endeavour to extinguish the fire.

If a fire has broken out in a space where no one is present and this room cannot be entered because of heat or smoke, set the door ajar and blow carbon dioxide into the room. Before entering the room protect yourself against smoke or lack of oxygen.

### GAS MASKS AND CANISTERS

**Using a gas mask**—Always use the proper canister and replace it (outside the danger zone) as soon as it transmits the harmful gas. Do not put off or shift the mask as long as you are in the danger zone. Select the proper canister with the aid of Tables 42, 45. Renew the canister as soon as it is exhausted. This is indicated by the smell of the transmitted gas or in some carbon monoxide filters by the smell of acetylene.

Deliver gas mask and canister immediately after use to the department where the mask is cleaned, sterilized and checked.

Since moisture has a detrimental effect upon the contents the canisters must be sealed when they are not being used. The masks should be stored in a cool room, in a place where the rubber will not be exposed to tension or direct sunlight.

Cleaning, checking and sterilizing of gas masks should exclusively be carried out by the person(s) appointed for this work.

**Maintenance**—When a gas mask has been used the canister is disconnected and the resistance checked. If the mask can be used again the openings must be sealed to protect the contents against moisture. The re-use of canister masks is not recommended. The lenses are taken out of the mask, cleaned and treated with an anti-misting agent. The face piece and connecting tube are washed with a soap solution, rinsed with water and sterilized. Chinosol and sagrotan can be recommended for this purpose. Subsequently the rubber parts are dried. Care should be taken to keep the temperature below 50° C.

The rubber parts of the valves are greased with a 10 per cent solution of glycerol in water. After the mask has been dried and the lenses screwed in again, it is stored in a dust-proof, cool, easily accessible space, preferably in the dark.

**Inspection and distribution**—Masks and canisters should be regularly inspected. Special attention should be paid to the condition of rubber parts, elasticity of the harness, buckles and joints of the harness, and to the canisters. When inspecting the canisters attention should be paid to damage due to corrosion.

The resistance should not exceed 20 mm water gauge at a velocity of 30 litres per minute. The time the canister has been in actual service should be well within the limit.



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The distribution, maintenance and inspection of gas masks and canisters as well as instruction and training should be assigned to one authorized person.

**Regeneration of carbon monoxide canisters**—Regeneration should be performed only by qualified personnel.

**Testing carbon monoxide canisters**—For 10 minutes air containing 1 per cent carbon monoxide by volume is passed through the canister at the rate of 15 litres per minute. The carbon monoxide content of the issuing air should not exceed 0.03 per cent by volume.

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## ANALYTICAL PROCEDURES RELATING TO TOXIC AND HAZARDOUS SUBSTANCES

**A**LTHOUGH many air contaminants can be detected by their odour or irritant effect, the sense of smell is rather subjective and may be temporarily impaired. It is therefore necessary to rely on objective methods. Analytical methods for the detection and quantitative determination of toxic substances must be sensitive and simple to perform. The apparatus must be simple and portable. Semi-micro techniques, especially colorimetric methods, are particularly suitable. Methods are based on refractivity (interferometer), heat conductivity (diaferometer) or absorption spectrum (spectrophotometer, infra-red analysis). Combustible gases in air can be detected and estimated by combustion on the surface of a platinum filament: the heat of reaction produces a temperature rise and a consequent change in electrical resistance of the platinum wire.

Special methods have been developed for certain substances. The detection of carbon monoxide for example is based on the heat of oxidation, when air containing carbon monoxide is passed over a catalyst and oxidized to carbon dioxide.

### DETECTION AND ESTIMATION OF SUBSTANCES INVOLVING FIRE AND EXPLOSION HAZARDS (TABLE 54)

#### DETERMINATION OF IGNITION TEMPERATURE OF SOLID FUEL BY KREULEN'S METHOD

**Principle**—The coal is heated slowly in a stream of oxygen. Due to the heat evolved by the oxidation of the coal its temperature rises more rapidly than the temperature of the apparatus. The ignition temperature is defined as the temperature of the coal at which the difference in temperature between coal and apparatus amounts to 6° C.

**Apparatus**—The assembly is shown in Figure 21 and consists of an oxygen cylinder with pressure regulator, a flow meter for the oxygen, an electric furnace with rheostat, a copper block with ground in cover and two thermometers for temperatures up to 400° C.



## IGNITION TEMPERATURE OF SOLID FUEL (COAL)

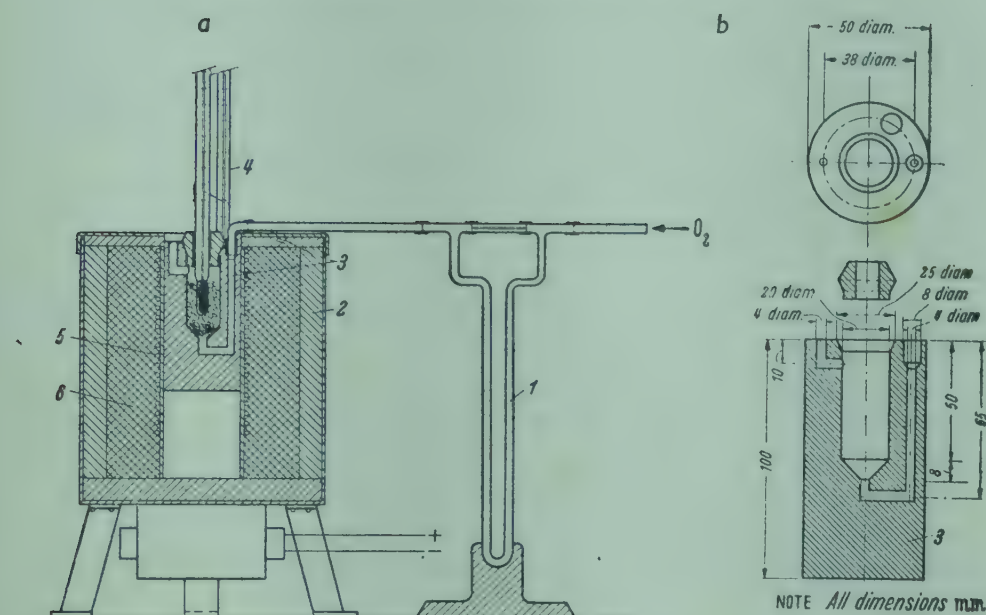


Figure 21. Apparatus for determining the ignition temperature of solid fuel : 1 flowmeter, 2 electric furnace, 3 copper block with ground in cover, 4 thermometers for temperatures up to  $400^{\circ}\text{C}$ , 5 heating coil, 6 insulating material.

### REAGENTS

**Coal sample**—The sample for this determination should meet the following requirements :

*a* its average composition should be identical to that of the laboratory sample

*b* it must have a standard particle size.

Grind the sample until it passes entirely through a  $0.125\text{ mm}$  diameter sieve, press the powder to briquettes in a pelleting press and crush these briquettes carefully in a mortar until the whole lot passes through a  $0.72\text{ mm}$  diameter sieve.

The fraction remaining on a  $0.3\text{ mm}$  diameter sieve is taken for the determination.

**Procedure**—Insert a plug of frayed asbestos cord into the copper block so that it rests on the outlet of the oxygen supply and put about  $5\text{ gm}$  of the treated sample on the asbestos. Fasten a thermometer through the cover of the copper block with the aid of asbestos cord, so that the mercury reservoir is at a distance of  $4\text{ cm}$  from the cover and place a second thermometer in the boring of the block. Close the block with the cover and put it in the furnace.

Switch on the electric current and heat to  $120^{\circ}\text{C}$  at the rate of  $3^{\circ}$  to  $5^{\circ}\text{C}$  per minute. Regulate the current in such a way that from  $120^{\circ}\text{C}$  onwards the temperature of the block rises at the rate of  $1^{\circ}$

**C** per minute. As soon as the temperature of the sample is  $4^{\circ}\text{C}$  below that of the block, pass oxygen through at the rate of 10 litre per hour. Read the temperatures on both thermometers every three minutes and record the temperature of the combustible which is  $6^{\circ}\text{C}$  higher than that of the block as the ignition temperature.

**Results**—The results are expressed within  $1^{\circ}\text{C}$  and should have a reproducibility within  $1^{\circ}\text{C}$ .

**Note**—Strictly speaking the fine material passed through a 93 mm diameter sieve should be briquetted and broken again. Experience has shown, however, that the omission of this second operation does not appreciably influence the result, provided the amount of fine material is not excessively large. This is attained by splitting the small briquettes in the mortar as carefully as possible.

The method also makes it possible to determine the ignition temperatures of greases and oils. For this purpose the material to be examined is mixed with pumice stone, particle size 0.3-0.71 mm.

## REINDERS' METHOD FOR DETERMINATION OF FLASH POINT OF HIGHLY INFLAMMABLE LIQUIDS

**Principle**—In the air just over the liquid a spark is generated. When this air contains a sufficient concentration of gaseous combustible material this spark causes an explosion which makes the disk with which the tube is loosely covered jump up. The highest temperature at which no perceptible displacement of the disk is observed is the upper flash point of the liquid.

**Apparatus**—The apparatus is illustrated in Figure 22. Further accessories of the apparatus are : millimeter paper, a transparent Dewar flask, a mercury thermometer (accuracy  $0.1^{\circ}\text{C}$ ), a stirrer or inlet tube extending to the bottom of the Dewar vessel, a barometer, an induction core connected to a battery of 4-6 v with a maximum spark length of 15-25 mm.

**Preliminary preparations**—Insert the clean and dry apparatus and the mercury thermometer in a vertical position into the Dewar flask. Fill the Dewar flask with alcohol to about 10 mm above the lower edge of the ground stopper. Remove the rubber stopper and the bent glass tube and transfer the sample to the U-tube by displacement of water until the liquid level reaches the mark *M*. Take care that the platinum does not come into contact with water. Replace the rubber stopper and the bent tube in their position and fix the millimeter paper behind the upper part of the capillary. Place the stirrer or inlet tube for air in the Dewar flask and add solid carbon dioxide until the temperature of the alcohol is about  $6^{\circ}\text{C}$  lower than the flash point. Maintain a uniform temperature by stirring or by



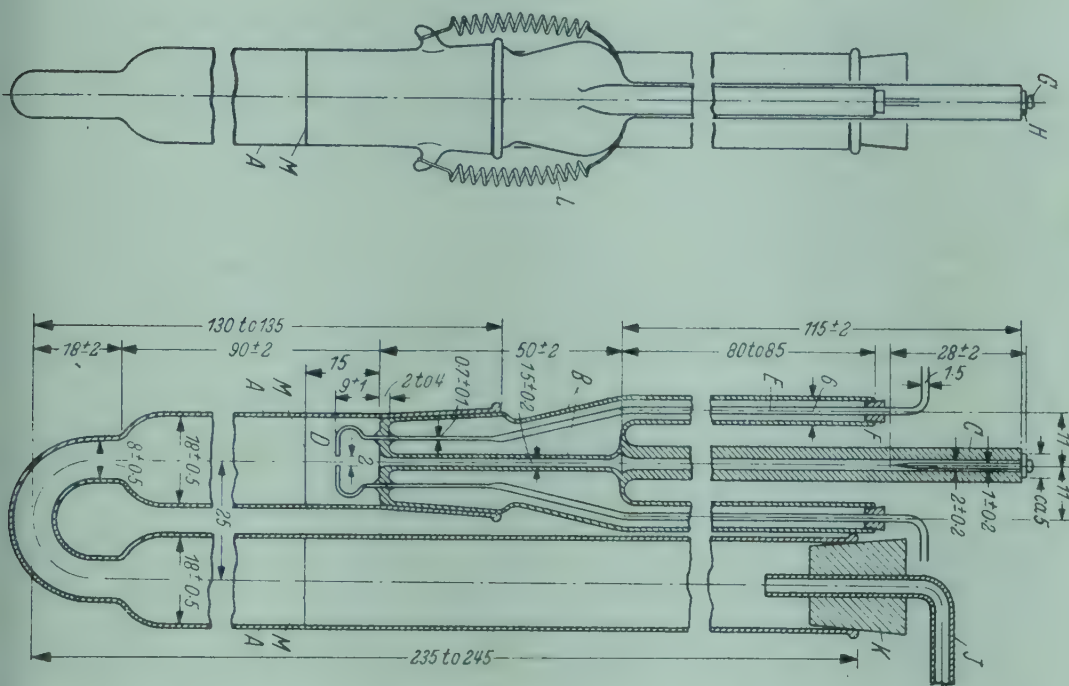


Figure 22. Apparatus for Reinders' method for determining flash point (dimensions in mm): *A* U-tube of pyrex or jena glass with a mark *M*, *B* ground hollow stopper with capillary boring, *C* capillary with smooth upper edge fused to *B*, *D*, *E*, Pt electrodes fused with *B*, *F*, copper wires soldered to *D*, *F*, rubber bungs, *G* pin, *H* disk of paper or celluloid (45-59 gm), *J* bent glass tube, *K* rubber bung, *L* metal spring holding *B* in place.

blowing in air. Connect the copper wires to the secondary terminals of the inductor and note the barometric height.

**Procedure**—By adding solid carbon dioxide and stirring, or blowing in air, maintain the bath of alcohol and carbon dioxide for five minutes at a constant temperature about  $5^{\circ}\text{C}$  lower than the flash point.

Then generate the shortest possible spark between the platinum electrodes and see if the pin and disk are thrown off, or to what extent the pin bearing the disk is pushed upwards. Read the distance on the millimeter paper. Remove disk and pin from the capillary and flush the space over the liquid twice with air by drawing the liquid twice into the long leg of the U-tube until the other level has dropped to the narrowed part of the U-tube and then allowing the liquid to flow back. Then replace the pin and the disk in position and, while stirring or blowing in air, allow the temperature of the mixture of alcohol and carbon dioxide to rise  $1^{\circ}\text{C}$ . Maintain this temperature for another five minutes and again generate the shortest possible spark, and read the displacement of pin and disk.

Repeat the experiment until the disk only manifests a slight shake which does not perceptibly diminish in two successive readings.

Plot the readings against the corresponding temperatures of the alcohol-carbon dioxide bath and note from this graph the temperature at which the pin with the disk rises 0.5 mm. If this temperature, in whole Centigrade degrees, is from 3° to 5° C higher than the temperature at which the first reading was noted, it is taken as the flash point of the liquid. If it is less than 3° C or more than 5° C higher the test should be repeated with a fresh amount of liquid, starting from a temperature which is 4° C lower than that found in the preliminary test.

**Note**—The result should include a note of the barometric pressure.

If the flash point is not roughly known its approximate value is determined by a preliminary test with a separate amount of liquid at decreasing temperatures, generating a spark at 20° C and multiples of 5° C less, and observing if explosion occurs. On no account should the test be commenced at an arbitrary temperature because of the hazard of a violent explosion which may damage the apparatus.

## DETERMINATION OF EXPLOSION LIMITS OF GASES

**Principle**—This method developed by PIETERS and RIETVELD permits continuous working. It has many advantages and saves a lot of time. The components of the gaseous mixtures are fed continuously in known quantities into the explosion tube, and as soon as the composition of the mixture in the tube becomes stationary the ignition spark is operated. Then the composition of the mixture is changed and in a few minutes another volume of gas flows through the explosion tube. In this way the explosive limits of a mixture can be determined in a very short time.

The relatively large diameter of the tube, 6 cm, diminishes the influence of wall effects. Further increase of the diameter does not affect the results. The influence of heat losses is diminished when the explosion is in an upward direction. Another factor which influences the explosion is the intensity of the spark: a spark of insufficient power does not ignite even an explosive mixture. The typical criterion of the explosion limit is that it does not change by increasing the intensity of the spark.

**Apparatus**—This is shown in Figure 23.

**Procedure**—The requisite volumes of each of the reaction components are measured and allowed to enter the explosion vessel 1 tangentially. They mix and flow downward through a layer of glass-wool 2 and finally pass the electrodes 3. The vessel 4 filled with glass-wool



prevents the explosion from propagating through the outlet tube. The explosion in 1 often causes the loosely fitting rubber stopper 13 to be expelled from the tube.

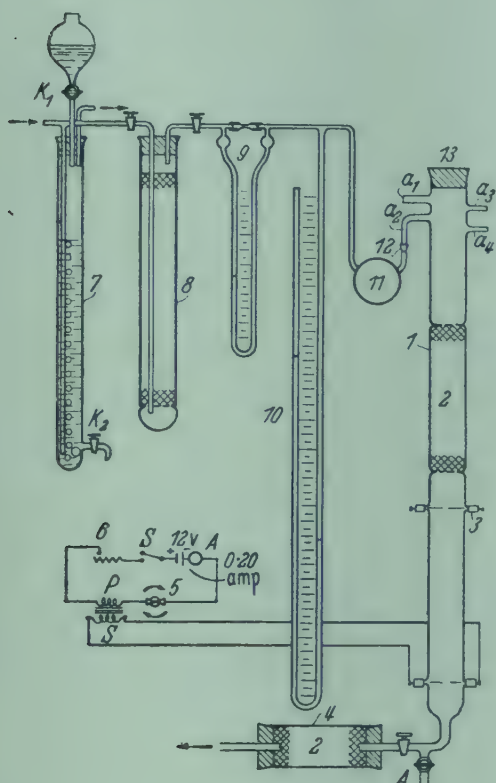


Figure 23. Determination of the explosion limits of gases : 1 explosion tube, 2 glass-wool, 3 electrodes, 4 flame extinguisher, 5 interrupter, 6 resistance, 7 pressure regulator, 8 drying tower, 9 flowmeter, 10 manometer, 11 gasmeter, 12 safety valve, 13 stopper,  $a^1$ — $a^4$  inlets for explosive components.

The mixture is ignited by a spark from a Ford induction coil. The primary current can be regulated by the resistance 6. The interrupter 5 revolves with a constant speed, which also can be adjusted. The distance between the electrodes can be fixed at 3, 5 and 7 mm. Every revolution of the interrupter produces two sparks. The best results were obtained when using the lower pair of electrodes and upward motion of the flame. The explosion limits are determined at first with a low intensity spark, and then the spark is intensified. This should not alter the result.

The flow of each of the components of the mixture is adjusted by using a pressure regulator 7 filled with a suitable liquid to a height which is adjusted by means of the taps shown in Figure 23. The excess gas bubbles through the liquid and escapes in the air or under the hood. The gas is dried in the drying tower 8. The gas stream is adjusted with a flowmeter 9. The inlet to the explosion tube is provided with a safety valve 12. The composition of the mixture can be controlled by analysing a sample, taken from the top before 4.

## DETECTION OF INFLAMMABLE GASES IN AIR

**M.S.A. Methane Detector**

**Principle**—The sample after passing through a tightly rolled copper gauze acting as a flame trap is divided into two streams, one of which passes through a combustion compartment, the other through a compensation compartment. The two streams unite in the aspiration line *via* a second copper gauze flame arrester. In the combustion compartment the air passes over an activated platinum wire, in the compensation compartment over a deactivated platinum wire. The two wires are heated to red heat by means of an electric current supplied by an accumulator. The wires form parts of a Wheatstone bridge which is adjusted so that, when pure air is passed, the galvanometer current is zero.

An inflammable gas present in the sample is oxidized at the surface of the hot activated platinum wire, the temperature of which rises. The resistance of the wire is thereby increased and the equilibrium of the Wheatstone bridge is disturbed, resulting in a deflection of the galvanometer, which is a measure of the concentration of the inflammable gas for which the galvanometer has been calibrated.

Since the volumes of air passing through the compensation and the combustion departments are equal the influences of variations in temperature, pressure and humidity of the sample are automatically eliminated. The apparatus responds quickly to the presence of inflammable gases in air, in concentrations far below the lower explosion limit.

**Apparatus**—The Mines Safety Appliances methane detector is illustrated in Figure 24.

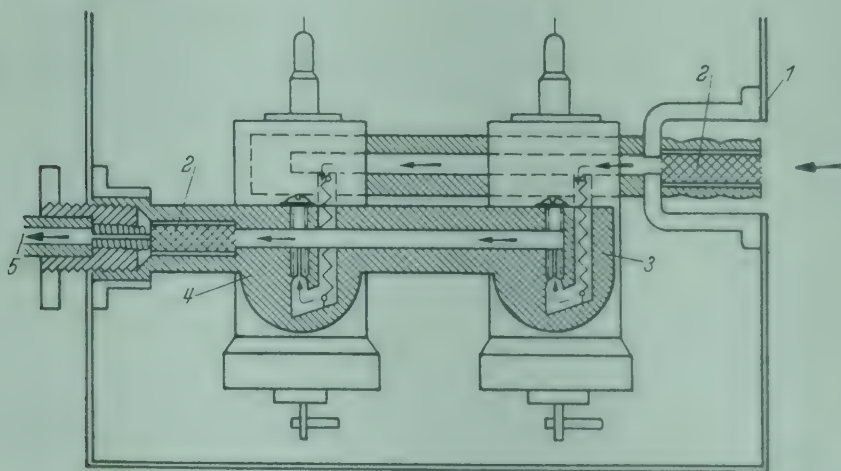


Figure 24. Section of the Mines Safety Appliances (Pittsburgh) methane detector : 1 gas inlet, 2 copper gauze flame traps, 3 combustion tube containing activated Pt wire, 4 compensation chamber containing deactivated Pt wire, 5 outlet to aspirator.



**DETECTION AND ESTIMATION OF ETHER PEROXIDE**

**Colorimetric methods**—Ether peroxide may be determined colorimetrically by the reaction with dichromate and sulphuric acid, with benzidine, with ferrous rhodanide, potassium iodide and starch or by the reaction with phenolphthalein.

**Benzidine test**—5 ml of a cold saturated solution of benzidine in water is mixed with 5 ml of a saturated sodium chloride solution and a few drops of a dilute solution of ferrous sulphate. Ether containing peroxide colours this mixture blue within a few minutes. When the peroxide content is high, the blue colour appears immediately.

**Ferrous-rhodanide test**—The reagent is prepared as follows : 30 ml of 10 per cent sulphuric acid is boiled while a stream of carbon dioxide is passed through. In the boiling liquid 5 gm of crystallized ferrous sulphate is dissolved. After cooling in a stream of carbon dioxide, 30 ml of 10 per cent potassium thiocyanate is added. The solution is reduced with 0.03 N titanous chloride at 40° C until it is colourless. The titanous chloride should be kept in an atmosphere of carbon dioxide and should be colourless.

30 ml of the ether and 5 ml of the reagent are shaken in a stoppered 35 ml flask. The intensity of the red coloration which develops after five minutes during which the solution is kept in the dark is an indication of the presence and the concentration of the peroxide. The sensitivity of this method amounts to 1 : 10<sup>7</sup>.

**Potassium iodide and starch test**—A brown colour is developed when potassium iodide and starch paper is dipped into ether containing peroxides.

**Phenolphthalein test**—This has been described by STAMM. The reagent is prepared as follows : 10 gm of sodium hydroxide dissolved in 20 ml of water is boiled with 1 gm of phenolphthalein and 5 gm of zinc dust until the liquid is colourless. The solution is then filtered through asbestos and diluted with water to 50 ml. The reagent should be kept in the dark.

The ether is shaken with 4 drops of the reagent, 3 ml of water and 5 drops of a 0.05 per cent copper sulphate solution. Alternatively 2 ml of water and 1 ml of ether is added carefully down the side of the test tube; a pink colour indicates peroxide.

**Titrimetric method**—This method depends on the liberation of iodine from potassium iodide, followed by titration with thiosulphate solution. Add 10 ml of ether to 150 ml of 2 N sulphuric acid in a conical flask and then add a few drops of a 1 per cent ammonium molybdate solution as catalyst followed by 15 ml of a 10 per cent

potassium iodide solution. Shake the flask and keep in the dark. After fifteen minutes titrate the free iodine with 0.05 N sodium thiosulphate solution.

## EXPLOSIVITY OF COAL DUST

**Principle**—The relative explosivity of coal dust is determined by the proportion of inert material required to prevent an explosion under standard conditions, the concentration of oxygen and the ignition temperature being kept constant.

**Apparatus**—The apparatus is illustrated in Figures 25 and 26. It is a modification of that used in the Godbert and Wheeler test.

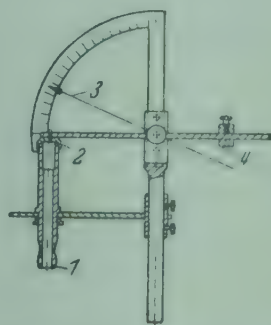
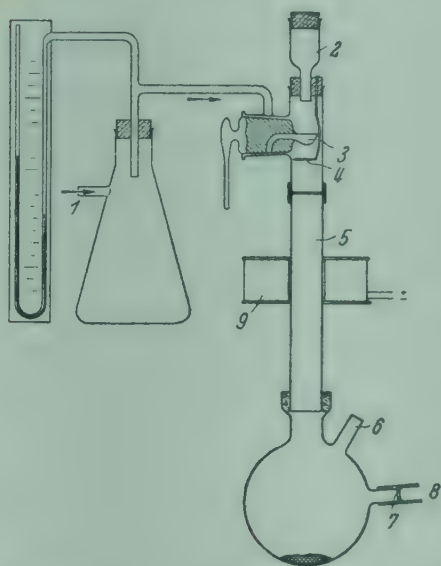


Figure 26. Apparatus for measuring explosion pressures : 1 nipple, 2 valve, 3 pointer, 4 weight.

Figure 25. Modified Godbert and Wheeler apparatus for determination of explosiveness of coal dust : 1 oxygen inlet, 2 dropping funnel, 3 sample tray in glass cock, 4 wire gauze to distribute sample, 5 quartz tube, 6 side tube for measuring explosion pressure, 7 exhaust diaphragm, 8 outlet tube, 9 furnace.

## REAGENT

A sufficiently large quantity of a powdered inert material such as powdered stone, marl or clay is required. A series of mixtures is made containing 0-80 per cent inert matter with the sample, increasing in intervals of 5 or 10 per cent.

**Sample**—The sample of coal is ground to pass a 75  $\mu$  screen. If the sample is already dust, it is passed through a 75  $\mu$  screen.

**Procedure**—Place 500 mg of the mixture of the coal and inert dust, both less than 75  $\mu$  diameter, in the tray attached to the cock. Regulate the oxygen pressure in the reservoir to 30 cm mercury. Heat the furnace to 900° C which corresponds to a temperature of 850° C in the tube. Open the cock quickly and note the result.



## DETECTION OF TOXIC GASES

After each experiment the tube is cleaned. The explosion limit is reached when the mixture burns with a large flame and a weak detonation.

**Results**—The flame type and explosion characteristics are indicated by the following symbolism :  $\alpha$  = no flame,  $\beta$  = small flame,  $\gamma$  = big flame,  $\gamma^+$  = big flame with weak detonation (explosion limit),  $\delta$  = big flame with detonation, and  $\epsilon$  = big flame with sharp detonation. Detonation is judged by the sound developed. The pressure set up by the explosion is registered on the manometer.

With each mixture four or five determinations are made. Each result is the average of five determinations.

**Note**—The explosion limit increases with increasing temperature. Below 750° C and above 950° C the reproducibility diminishes : 900° C is to be preferred.

Between 20 and 10 cm Hg of oxygen pressure the explosion limit does not change with the pressure of the oxygen ; 30 cm is preferable.

The explosion limit increases a little when the diaphragm is smaller. The apparatus to measure the explosion pressures requires a diaphragm of 4 to 6 mm. The average error is less than 2 per cent.

It is of great importance to express the results of the experiments in simple relations. The relation established by GODBERT and WHEELER between the percentage of inert material  $S$  required to suppress the explosivity of the cloud and the percentage of volatile matter  $V$  of a coal is :

$$S = 100 - \frac{1,250}{V}$$

This relation is based on the result of experiments in a test gallery, where coal dust of 12·5 per cent volatile matter proved to be non-explosive. Further experiments on a sufficiently large scale and with different types of coal will have to be made before this relation can be generally accepted. Relations based on the energy released by the explosion have not been sufficiently confirmed.

## DETECTION AND DETERMINATION OF TOXIC SUBSTANCES IN AIR (TABLES 54-56)

### DETECTION OF TOXIC GASES

The methods are based on the formation of a coloured compound when the contaminated air is drawn by means of a hand pump through strips of filter paper clamped in a holder, or through a small wash bottle (Figure 28). The filter paper is soaked with the reagent solution and dried ; the wash bottle contains a solution of the reagent.



Figure 27. Hand pump for drawing contaminated air over test paper: 1 counter, 2 holder for reagent paper, 3 rubber packing.

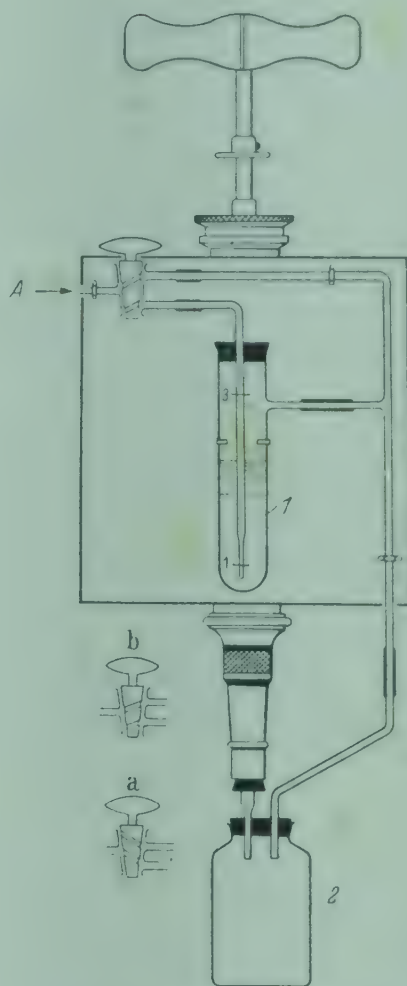


Figure 28. Pump arranged for drawing air through wash bottle: 1 absorption vessel, 2 drop arrester, a, b, alternative positions of stopcock.

The intensity of the colour is a function of the volume of air passed through the reagent and the concentration of the contaminant. The colours are compared with a colour chart or with colours developed with a standard solution. To test places which are not readily accessible or where the concentration of the toxic gas is relatively high and therefore hazardous, the contaminated air is sampled through a dry glass tube connected with the inlet of the pump.



## CARBON DISULPHIDE

The chemicals used for the preparation of the reagent should be of chemically pure (*Analar*) quality. The test paper is prepared by soaking slips of filter paper with the reagent. When dry, the slips are trimmed and cut into strips. In large rooms several tests should be made at various places in order to get a reasonable average.

## AMMONIA

The ammonia contained in a known volume of the air is absorbed in dilute sulphuric acid. The ammonium content of this acid is subsequently determined by alkalimetric titration or colorimetrically with Nessler's reagent.

## ARSINE

**Principle**—Arsine produces a stain on a mercuric chloride test paper, and by comparing the stain with a standard chart the concentration of arsine can be estimated (Table 54, p 237).

### REAGENTS

*Test paper*—Strips of filter paper are immersed in a 5 per cent mercuric chloride solution, drained and dried. The paper is cut up, the ends are discarded and the strips kept in a stoppered bottle.

**Procedure**—Draw the air through the test paper and compare with the standard chart within 5 minutes after the test.

**Result**—The result is expressed as 1 volume of arsine in  $x$  volumes of air.

## CARBON DISULPHIDE

**Principle**—Carbon disulphide produces a coloured product with a solution of diethylamine and copper acetate.

### REAGENTS

*Diethylamine*—2 ml diethylamine is dissolved in 100 ml benzene.

*Copper acetate*—100 mg copper acetate is dissolved in 100 ml 96 per cent alcohol.

*Alcohol*—96 per cent.

*Standard*—1 ml carbon disulphide is made up with alcohol to 100 ml and 1 ml of this solution is made up with alcohol to 50 ml.

**Procedure**—Measure in turn 10 ml alcohol, 2 ml diethylamine solution and 2 ml copper acetate solution into the bubbler.

Transfer 0.25, 0.50, 1.0 and 2.0 ml of the standard into tubes of the same diameter as the bubbler, make up each to 10 ml with alcohol and add to each 2 ml diethylamine and copper acetate solutions. Allow the mixtures to stand in the dark for 15 minutes for the full development of the colours.

Connect the bubbler to the pump and draw the air slowly and steadily through the reagent (1 stroke per 10 sec). Remove the bubbler and allow to stand for 15 minutes before comparison is made with the standard colours.

**Result**—The result is expressed as 1 volume of carbon disulphide in  $x$  volumes of air with the aid of Table 21.

**Note**—Hydrogen sulphide interferes; traces can be removed by drawing the air through lead acetate paper.

Table 21. Data for CS<sub>2</sub> Determination

CS <sub>2</sub> solution ml	0.25	0.5	1.0	2.0
No. of pump strokes	$x$			
1	6,000	3,000	1,500	750
2	12,000	6,000	3,000	1,500
3	18,000	9,000	4,500	2,300
5	30,000	15,000	7,500	3,800
20	120,000	60,000	30,000	15,000

## DETECTION AND ESTIMATION OF CARBON MONOXIDE IN AIR

(TABLE 54, pp 238, 239)

In concentrations above 0.5 per cent by volume the carbon monoxide can be determined by absorption in a gas pipette using a solution of ammoniacal cuprous chloride or cuprous sulphate with 2-naphthol or preferably a suspension of iodine pentoxide in fuming sulphuric acid. With a special pipette concentrations down to 0.2 per cent by volume can be analysed with reasonable accuracy (Figure 29).

Lower concentrations can be determined as follows :—

**Colorimetrically**—With iodine pentoxide and oleum on pumice, palladium sulphate and ammonium molybdate on silica gel, palladiumchloride, or with blood and tannic acid.

**Titrimetrically**—The air is passed over heated iodine pentoxide which oxidizes the carbon monoxide quantitatively to carbon dioxide, liberating an equivalent amount of iodine. The iodine or the carbon dioxide can be titrated, or the carbon dioxide can be absorbed and weighed.

**Oxidation by hopcalite**—The carbon monoxide is oxidized to carbon dioxide, which can be titrated. The carbon monoxide content of

## DETECTION AND ESTIMATION OF CARBON MONOXIDE

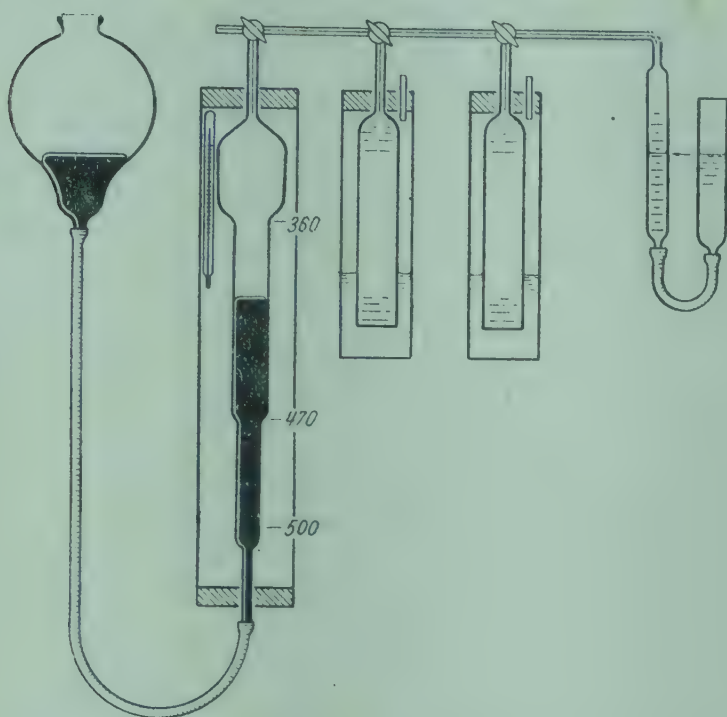
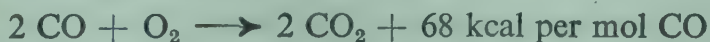


Figure 29. Apparatus for titrimetric determination of carbon monoxide by reaction with iodine pentoxide in fuming sulphuric acid.

the air can also be derived from the rise in temperature caused by the heat effect of the reaction :

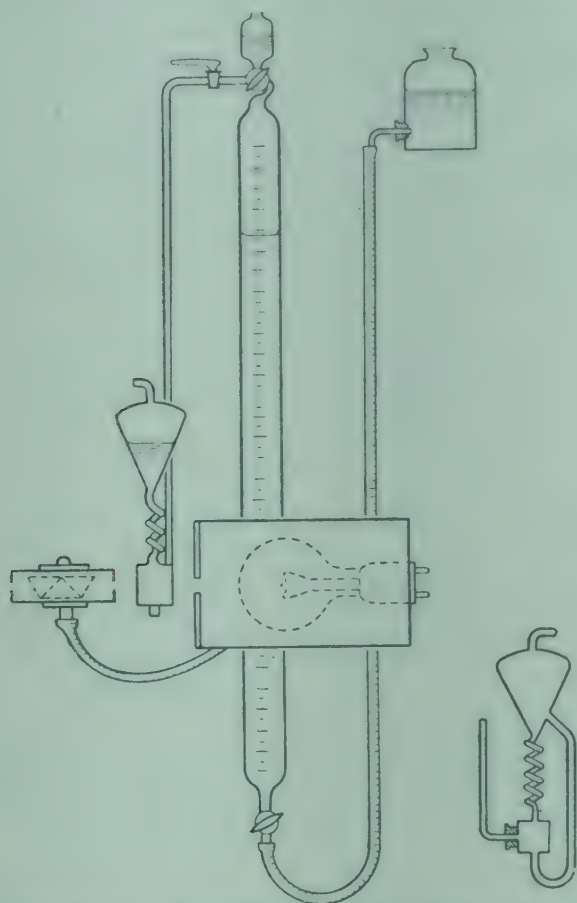


Hopcalite is a mixture of 50 per cent  $\text{MnO}_2$ , 30 per cent  $\text{CuO}$ , 15 per cent  $\text{Co}_2\text{O}_3$  and 5 per cent  $\text{Ag}_2\text{O}$  or of 60 per cent  $\text{MnO}_2$  and 40 per cent  $\text{CuO}$ . KATZ and KATZMAN use granular silver permanganate on a zinc oxide carrier as catalyst for the oxidation of carbon monoxide at room temperature.

**Oxidation by mercuric oxide**—The carbon monoxide is oxidized to carbon dioxide by passage over heated mercuric oxide and an equivalent amount of mercury is liberated. The carbon dioxide can then be determined. Low concentrations of carbon monoxide can be detected by a colorimetric determination of the mercury.

**Spectrographically**—The characteristics of the absorption spectrum of the compound of carbon monoxide and haemoglobin permit the carbon monoxide to be determined in concentrations as low as from 0.1 to 0.0001 per cent by volume. The apparatus is outlined in Figure 30 and shown in more detail in Figure 34.





**Figure 30.** Apparatus for determining carbon monoxide by the haemoglobin method.

## COLORIMETRIC METHODS

### (A) WITH IODINE PENTOXIDE

The method is based on the temporary colour reaction produced by small amounts of carbon monoxide with a suspension of iodine pentoxide in fuming sulphuric acid.

The reagent named hoolamite by HOOVER and LAMB, who developed it, is applied on granular pumice stone which serves as a carrier.

Its composition is said to be as follows :  $\text{I}_2\text{O}_5$  12 per cent, sulphuric acid, containing 47 per cent  $\text{SO}_3$ , 52 per cent, granular pumice stone 36 per cent. The reagent is hygroscopic and is supplied in sealed tubes.

All gases which liberate iodine from iodine pentoxide interfere with the determination *e.g.* acetylene, alcohol, ammonia, benzene, ether, ethylene, petroleum, hydrogen sulphide and hydrochloric acid, and in order to eliminate these interfering substances the air is passed through activated charcoal.

## COLORIMETRIC METHODS

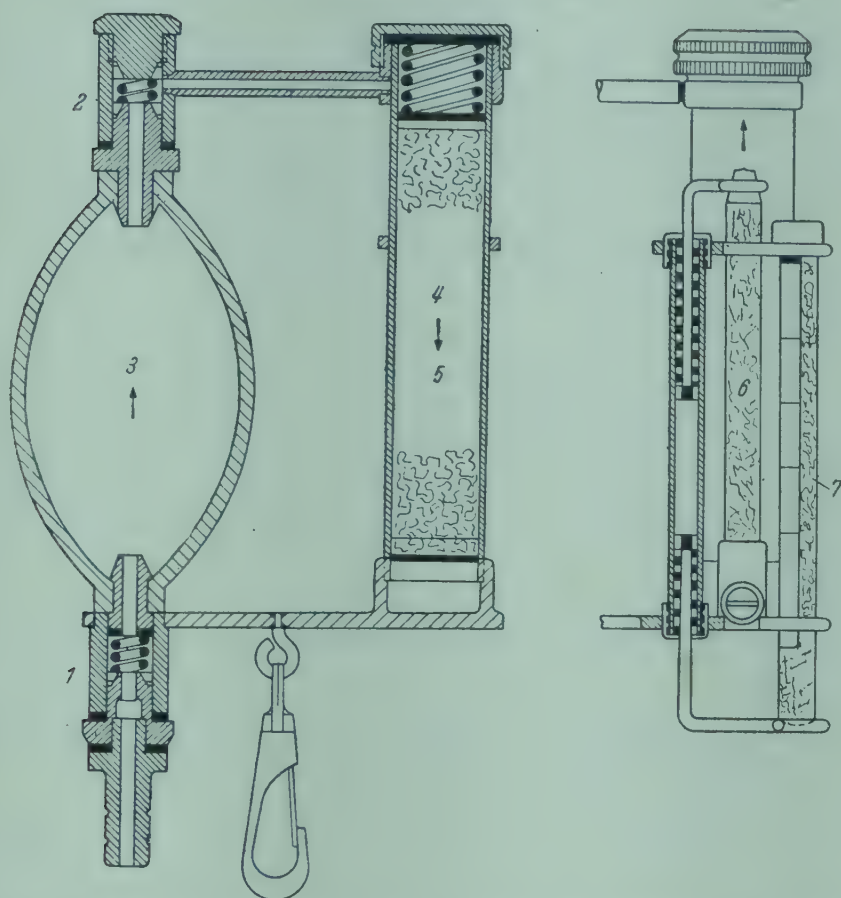


Figure 31. Mines Safety Appliances (Pittsburgh) apparatus for detection of carbon monoxide in the atmosphere : 1 suction valve with filter, 2 pressure valve, 3 aspirator bulb, 4 activated charcoal to absorb organic vapours, 5 wadding, 6 glass tube containing hoolamite, 7 comparison tube with standard colour scales.

The carbon monoxide reacts with the iodine pentoxide according to the equation :



The liberated iodine produces a green coloration which disappears after some time. Within certain limits (0.1—2.0 per cent by volume) the carbon monoxide content present in the air can be determined from the colour intensity and the volume of air passed through the reagent.

**Apparatus**—The apparatus consists of a hand pump, a tube filled with activated charcoal and the tubes containing hoolamite (Figure 31).

When the air is passed through the reagent some sulphur trioxide escapes.

**Procedure**—Ascertain whether the valve is properly set. Inspect the pump, or aspirator bulb, the functioning of the valves and the

activated charcoal. Pass pure air through a hoolamite tube and renew the activated charcoal if after twenty strokes of the pump the tube shows a coloration.

Squeeze the aspirator bulb a few times, break off the ends of a new hoolamite tube and insert in the apparatus. Compare the colour of the hoolamite tube with the standard chart after every 10 deflations of the aspirator bulb. Repeat the test with a fresh hoolamite tube. Remove the hoolamite tube from the apparatus after the test has been completed.

**Note**—The comparison of the colours may sometimes be difficult. Whereas the entire contents of the hoolamite tube may in one test be coloured homogeneously, a local coloration may be produced in other cases. From this it follows that the reagent is not always homogeneous. With carbon monoxide content greater than 0.5 per cent by volume a green coloration is quickly produced after a few strokes of the pump.

A negative result of the test does not imply that no carbon monoxide is present, hence the test should always be repeated with a fresh hoolamite tube.

Carbon monoxide concentrations below 0.05 per cent by volume cannot be detected with accuracy by this method.

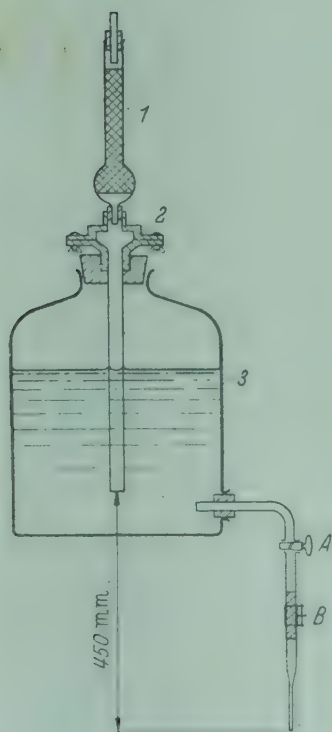


Figure 23. Apparatus using palladium chloride for detection of carbon monoxide: 1 tube filled with activated charcoal in air, 2 test paper holder, 3 aspirator.



(B) WITH PALLADIUM CHLORIDE

**Principle**—The air is passed through a filter paper which has been treated with palladium chloride. In the presence of carbon monoxide a stain is produced. The carbon monoxide content can be calculated from the volume of air passed through the paper and the intensity of the stain.

**Apparatus**—This is illustrated in Figure 32 and comprises a tube filled with activated charcoal, a holder for the test paper, and a 5 litre aspirator.

REAGENTS

*Palladium chloride test paper*—This should be prepared immediately before use. 0.1 gm of palladium chloride is boiled for some minutes in 20 ml of water, and filtered. The filtrate is cooled and diluted with water to 20 ml. 20 ml of acetone is added while stirring. The filter paper is immersed in the solution for 1 minute, allowed to drain and pressed between sheets of filter paper. The solution will keep for some time. If the solution becomes turbid it should be discarded.

*Activated charcoal.*

**Procedure**—Fill the aspirator with water. Open tap A and adjust the discharge by means of the screw clip B so that it gives a flow of 45 to 55 ml per minute. Close tap A and clamp the test paper in the holder. Open tap A and draw the air through the test paper for 2 minutes. Close tap and compare the colour of the test paper with the standard colours. Repeat this procedure until a colour is obtained intermediate between the standard colours. Note the total sampling time, and repeat the test without interruption, using a fresh test paper and taking slightly less time than in the preliminary test.

**Results**—The results are expressed in 1 part by volume of CO per  $x$  parts by volume of air. Read the concentration as a function of the time from the chart.

**Note**—The tube which is connected with the holder for the test paper should extend to near the bottom of the aspirator and must always be kept under water.

The activated charcoal should be renewed after 250 tests.

(C) WITH POTASSIUM PALLADIUM SULPHITE<sup>1</sup>

**Principle**—The indicating gel reacts with carbon monoxide, producing a brown coloration. This reaction is practically instantaneous. The length of the brown column formed is a measure of the amount of carbon monoxide present in the sample. Moisture and hydrocarbons that would interfere with the determination are retained in a guard gel.

## REAGENT

The indicator tube, 12 mm in diameter, contains a column of 2-3 cm silica gel sensitized with potassium palladium sulphite with on either side a column of 5-6 cm pure silica gel.

**Procedure**—Draw a definite volume of the sample at a moderate rate through the indicating tube by means of a double aspirator. Compare the length of the brown coloration with those produced by standards.

**Note**—When using the double aspirator, carbon monoxide concentrations as small as 0.001 per cent already produce a perceptible brown coloration and concentrations of from 0.001 per cent to 0.1 per cent can be determined with sufficient accuracy.

Since the air may be passed in either direction through the indicating tube each tube can be used twice. The indicating gel is not entirely insensitive to hydrogen.

(D) WITH SILICO MOLYBDIC ACID<sup>2</sup>

**Principle**—The indicating gel reacts with carbon monoxide and turns green to blue. The colour shade is a measure of the carbon monoxide concentration. The reaction does not proceed very rapidly so that when the sample is drawn through at a sufficiently high rate the colour response also depends on the time. The velocity with which the sample is passed through the indicator therefore must be standardized. This method is accurate and recommended as a field test for low concentrations.

## REAGENT

The indicating tube, 7 mm in outside diameter and 12 cm long, is filled alternately with 5 cm pure silica gel, 1-1.5 cm indicating gel, consisting of silica gel impregnated with silico molybdic acid which has been activated with palladium sulphate, and another 2 cm pure silica gel.

**Procedure**—Draw the sample, by means of a rubber bladder, through the indicating tube *via* an orifice for a definite period. Compare the colour of the indicating gel with and read the concentration from the colour chart. As a rule the sample is drawn through once; with low concentrations two to five times.

**Note**—Concentrations of from 0.001 to 0.1 per cent can be determined by this method. Hydrogen does not interfere.

TITRIMETRIC DETERMINATION OF CARBON MONOXIDE AFTER OXIDATION  
WITH IODINE PENTOXIDE

**Principle**—The air is passed through a tube filled with iodine pentoxide which is kept at a temperature of 100° C. The carbon monoxide is oxidized to carbon dioxide which is absorbed in a known quantity of barium hydroxide, the excess of which is titrated.

## COLORIMETRIC METHODS

The iodine liberated during the reaction is retained in a tube filled with silver wool, heated at  $250^{\circ}\text{C}$ .

### Apparatus

This is illustrated in Figure 33.

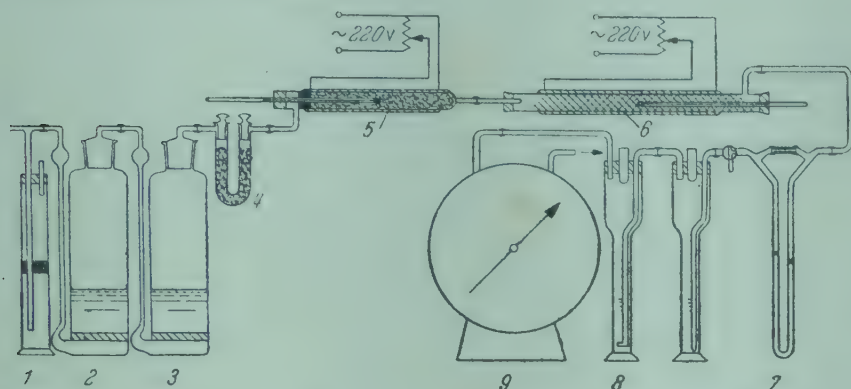


Figure 33. Apparatus for the titrimetric determination of small amounts of carbon monoxide in air by oxidation with iodine pentoxide : 1 mercury filled pressure regulator and safety valve, 2 wash bottle with 6N KOH, 3 wash bottle with  $\text{H}_2\text{SO}_4$  sp gr 1.84, 4 U-tube with  $\text{P}_2\text{O}_5$ , 5  $\text{I}_2\text{O}_5$  tube in furnace at  $100^{\circ}\text{C}$ , 6 Ag wool tube in furnace at  $250^{\circ}\text{C}$ , 7 flowmeter, 8 absorption vessels with  $\text{Ba}(\text{OH})_2$ , 9 gasmeter.

## REAGENTS

*Mercury*

*Potassium hydroxide solution 6 N*

*Sulphuric acid sp gr 1.84*

*Magnesium perchlorate*

*Iodine pentoxide, sieve fraction 1—2.8 mm*

*Silver wool*

*Barium hydroxide, standardized*

*Hydrochloric acid, standardized, c 0.05 N*

*Phenolphthalein.*

**Sample**—The air should be free from hydrocarbons since these react with iodine pentoxide. The volume passed should be so large that at least 3 ml of barium hydroxide is neutralized.

**Procedure**—First check over the apparatus. Heat the furnaces containing the iodine pentoxide and silver wool to  $100^{\circ}\text{C}$  and  $250^{\circ}\text{C}$  respectively. Replace the absorption vessels by a tube filled with calcium chloride. Pass a stream of nitrogen through the apparatus and determine the weight of the calcium chloride tube every half hour until this weight does not change more than 0.5 mg. 14

Then proceed with the analysis. Expel the nitrogen from the apparatus by passing the sample through for 10 min at a velocity of about 30 litres per hour. Allow the gas to escape through the three way cock. In the meantime fill the absorption vessels with air



free from carbon dioxide and measure 20 ml of barium hydroxide into each vessel. Close the absorption vessels, connect them with the apparatus and take the reading of the gas meter. Decrease the velocity of the gas stream to 6 litres per hour and turn the three way cock so that the gas stream passes through the absorption vessels.

After a suitable amount of gas has been passed, cut out the absorption vessels by means of the three way cock and take the reading of the gas meter.

Add 2 drops of phenolphthalein to the barium hydroxide and titrate with hydrochloric acid in a stream of air free from carbon dioxide. Towards the end of the titration the liquid should be drawn into the inlet tube a few times and titrated until the liquid becomes colourless. A blank experiment with 20 ml of barium hydroxide should be performed in a similar manner.

**Results**—The carbon monoxide content is calculated in per cent by volume using the formula :

$$p = 2 \frac{1.12 (v_0 - v)t}{V}$$

in which  $V$  = volume of gas passed,  $v_0$  = ml of hydrochloric acid used in the blank,  $v$  = ml of hydrochloric acid used in the test,  $t$  = titre of the hydrochloric acid ; the result being expressed to two decimal places.

**Note**—The first of the two absorption vessels has no glass filter in order to prevent obstructions to barium carbonate : the second however is provided with one for the purpose of effecting complete absorption of the carbon dioxide. After the test has been completed the gas is expelled by means of a stream of dry nitrogen.

When the apparatus is used regularly it is advisable to keep the furnaces at the required temperatures. When a series of tests has to be carried out, the gas for the following test may be used to sweep the apparatus.

#### SPECTROSCOPIC DETERMINATION OF CARBON MONOXIDE USING HAEMOGLOBIN

**Principle**—The absorption spectrum of a haemoglobin solution shows a dark band in the green part of the spectrum. As soon as about 30 per cent of the haemoglobin is saturated with carbon monoxide the dark band splits. This method is specific for CO.

When gas containing carbon monoxide is passed through a given quantity of haemoglobin the amount of gas which has to be passed before this splitting occurs is a function of the carbon monoxide concentration. The carbon monoxide content of an unknown sample can be derived with the aid of a calibration curve prepared with samples of known carbon monoxide contents.

While the gas is passed through the haemoglobin solution, the carbon monoxide is only partly absorbed, in amount depending on the dimensions of the absorption vessel, the amount of haemoglobin and the velocity at which the gas is passed. Consequently each absorption vessel has its own reference curve and the circumstances of the test must be standardized.

Nitrous oxide and oxygen are also bound by the haemoglobin and produce a splitting of the absorption band. These gases are removed with the aid of an alkaline solution of sodium hyposulphite,  $\text{Na}_2\text{S}_2\text{O}_4$ .

### Apparatus

The apparatus is illustrated in Figure 34.

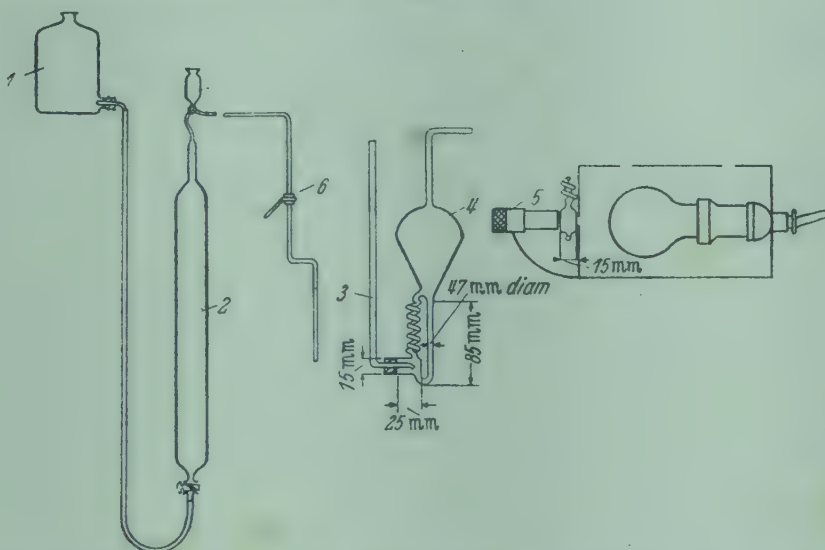


Figure 34. Apparatus for the spectroscopic determination of carbon monoxide in air using haemoglobin solution : 1 levelling bottle, 1 litre, 2 gas burette, 1 litre, 3 capillary tube, 4 absorption vessel, 5 spectroscope with lamp, 6 regulating cock.

### REAGENTS

**Haemoglobin solution**—1.25 gm haemoglobin is dissolved in 200 ml of boiled water in a 250 ml measuring flask. 25 ml of alcohol 96 per cent is added with shaking, and shaking is continued for 1 hr. The volume is made up to 250 ml with boiled water and the solution filtered through cotton. The solution should be kept in a stoppered flask and may only be used as long as it remains clear.

**0.2 N ammonia**

**Sodium hyposulphite,  $\text{Na}_2\text{S}_2\text{O}_4$**

**Saturated sodium hydroxide solution.**

**Sample**—A sample of 500 ml is used. The gas to be tested should not contain more than 1 per cent by volume of carbon monoxide.

**Preliminary procedure**—Connect the sample bottle with a levelling bottle filled with a sealing liquid and expel about 50 ml of gas.

Bring the gas to atmospheric pressure with the levelling bottle and note the level of the liquid on the bottle. Then draw the greater part of the liquid from the bottle so that a reduced pressure is created. In doing so, take care that no gas can escape.

Introduce a solution of 20 mg sodium hyposulphite and 20 ml saturated sodium hydroxide solution in 80 ml water, draw into the bottle and shake for 6 minutes to absorb oxygen and nitrous oxide. Adjust the gas to atmospheric pressure and note the level of the liquid in the bottle. Transfer the gas into a burette and determine the volume of the gas before,  $v_0$ , and after,  $v$ , absorption of the oxygen and nitrous oxide by filling the bottle up to the mark and weighing it.

**Determination**—If the CO-content of the gas lies between 0.1 and 0.01 per cent by volume, 6.0 ml of haemoglobin solution, 1.0 ml of ammonia and 100 mg of  $\text{Na}_2\text{S}_2\text{O}_4$  are measured into the absorption vessel. If the CO-content is less than 0.01 per cent by volume, 3.0 ml haemoglobin solution, 3.0 ml water, 1.0 ml ammonia and 100 mg  $\text{Na}_2\text{S}_2\text{O}_4$  are used.

Bring the gas in the burette under pressure by means of the levelling bottle, open the cock and flush the connecting tube with the gas. Close the cock and connect the tube with the absorption vessel. Bring the gas in the burette to atmospheric pressure and note the volume  $v_1$ . Bring the gas under pressure, open the cock and pass the gas through the absorption vessel at the rate of two bubbles per second. Close the cock as soon as the absorption band is split. Bring the gas in the burette to atmospheric pressure and read the volume  $v_2$ .

**Calibration**—The curve  $c = f(v)$  can be determined with oxygen free gas samples of known carbon monoxide content, in accordance with the method described above, where  $c$  = CO-content in per cent by volume,  $v = (v_1 - v_2)$  = volume in ml of gas passed.

**Results**—The carbon monoxide content of the gas is calculated in per cent by volume using the formula :

$$p = c(v_0' / v_0)$$

where  $c$  is the CO-content in per cent by volume of the gas, derived from the calibration curve, and  $v_0$  and  $v_0'$  represent the values found in the preliminary experiment.

The results are expressed within 0.001 per cent by volume if the carbon monoxide content of the gas ranges from 0.1 to 0.01 per cent by volume : 0.0001 per cent if the carbon monoxide content of the gas is less than 0.01 per cent by volume.

**Note**—The absorption band splits gradually. All determinations should be based on the same degree of splitting *i.e.* they should be performed by the analyst who did the calibration.



If the oxygen content of the gas is less than 1 per cent by volume, the preliminary work is not necessary, since the amount of sodium hyposulphite in the haemoglobin solution is sufficient to bind this oxygen.

#### MICRODETERMINATION OF CARBON MONOXIDE IN AIR USING SELENIUM SULPHIDE PAPER

**Principle**—Carbon monoxide is oxidized by mercuric oxide to give an equivalent amount of mercury vapour. The mercury reacts with selenium sulphide paper :



thus producing a black coloration over a length which is a measure of the amount of carbon monoxide.

#### Apparatus

The apparatus is shown in Figures 35 and 36.

#### REAGENTS

*Selenium*

*Hydrochloric acid* sp gr 1.19

*Nitric acid* sp gr 1.4

*3 N solution potassium cyanide*

*Red mercuric oxide*

*Hydrogen sulphide*

*Methanol*

*Ice*

*Standard mixture of air* containing 0.010 per cent carbon monoxide by volume

*Filter paper, Machory 530* or equivalent quality.

#### PREPARATION OF REAGENTS

**Selenium**—Moisten the selenium with methanol and dissolve in an excess of potassium cyanide. Heat the solution for half an hour on an electric hot plate and filter through a folded paper filter. Cool the filtrate and add an equal amount of crushed ice. While stirring continuously add an excess of cooled hydrochloric acid. Adequate ventilation is essential as hydrogen cyanide is evolved. This should be carried out in a fume chamber.

Wash the selenium with water in a Büchner funnel until the smell of hydrogen cyanide has disappeared, and then wash a few times with methanol. Dry at 110-130° C and pulverize in a mortar.

**Selenium dioxide**—The purified selenium is dissolved in nitric acid and evaporated to dryness in a porcelain dish on a water bath. Heat the residue for 1-2 hours at 140-150° C to give the white selenium dioxide.

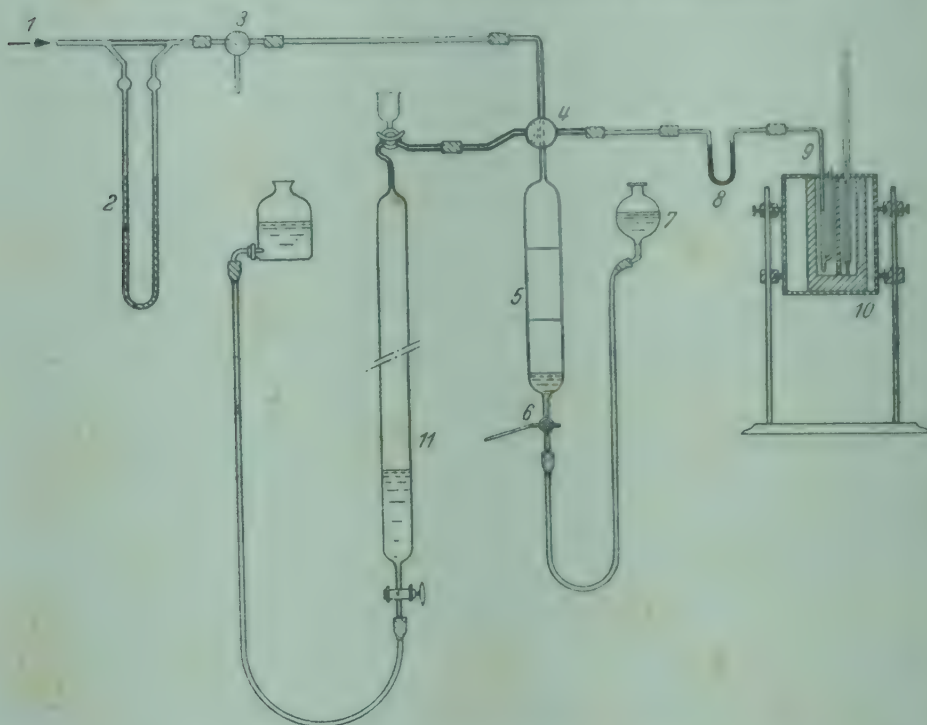


Figure 35. Apparatus for determination of carbon monoxide in air using selenium sulphide paper : 1 compressed air inlet, 2 flow meter, 3 three-way cock, 4 four-way cock, 5 gas pipette, 6 regulating cock, 7 levelling bulb filled with acidified water, 8 carbon filter, 9 reaction tube, 10 electric furnace, 250° C, 11 burette containing standard mixture.

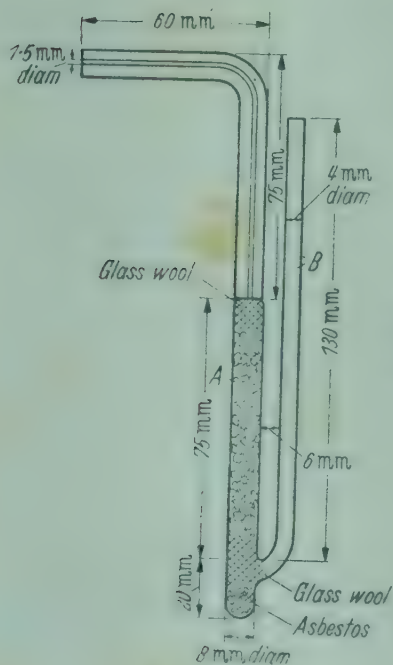


Figure 36. Pyrex reaction tube for determination of carbon monoxide : A red mercuric oxide, B selenium sulphide test paper in reaction tube.

**Preparation and storage of test papers**—A strong thin filter paper is used. The amount of reagent to be absorbed by the paper depends on the kind of paper and on the concentration of the selenium dioxide solution. For a given paper the concentration of the selenium dioxide solution must be determined experimentally so that 0.01 per cent carbon monoxide by volume will produce a coloration over a length of *c* 30 cm. Filter paper *Machory 530* soaked in 0.025 molar selenium dioxide produced a coloration over a length of 30 cm.

The paper is cut into pieces 20 cm square. Fold down a strip 1 cm wide and fasten with staples. Insert a stiff chromel wire under the folded part and immerse the strips for 10-15 minutes in the selenium dioxide solution. Hang the strips horizontally on chromel wire to drain until they no longer drip but are not yet dry, and expose the moist strips to a stream of hydrogen sulphide for 10-15 minutes. Hang the strips in a well ventilated place to dry at room temperature, away from direct sunlight. When the strips are dry remove wires and staples and press the strips flat.

To stabilize the strips wrap them in a sheet of thick filter paper to prevent evaporation of selenium sulphide during heating. Heat strips at 140° C for half an hour with frequent turning.

Only the middle part of the impregnated strips has a homogeneous selenium sulphide content over an area of  $17.5 \times 12.5$  cm. Trace this area on the strip with a pencil so that the long side of the rectangle runs parallel to the folded side of the paper. Cut this homogeneous part into strips 3.0 mm wide and 12.5 cm long.

**Red Mercuric Oxide**—Dissolve mercury in nitric acid and evaporate to dryness in a porcelain dish on a water bath. Heat the residue gently with a gas flame. Remove the burner after the liberation of nitrous fumes has almost ceased and allow to cool. Break the cake into lumps, avoiding pulverization. Heat the dish for 3-5 minutes to near red heat and stir. Allow to cool and resume the heating until the whole contents are converted to mercuric oxide having an orange colour at room temperature. Sieve the mercuric oxide to a grain size of 1.2—2.4 mm.

**Sample**—For every determination 250 ml gas is required. The sample should not contain over 0.03 per cent carbon monoxide by volume. Air with a higher concentration of carbon monoxide is diluted with nitrogen or with CO-free air. Hydrogen interferes. Heavy hydrocarbons and aromatics also interfere and are removed by active carbon.

### Procedure

**Arrangement of apparatus**—Fill tube A with mercuric oxide (Figure 36) and seal the tube close to the asbestos. The apparatus is as indicated by Figure 35.



Heat the furnace to 250° C and pass air through the reaction tube (Figure 36) at the rate of 10-12 litres per hour for three hours to activate the mercuric oxide. Shut off the air stream and lower the furnace slowly until the reaction tube is free.

**Blank test**—Heat the reaction tube to 163-165° C. Fill the gas pipette to the lowest mark (50 ml) with CO-free air. Insert a selenium sulphide test strip in the reaction tube and pass the gas over the mercuric oxide at a rate to displace the contents of the gas pipette in three minutes. Observe the test strip ; if it reveals black coloration the operation is repeated with another quantity of air until no coloration appears.

**Calibration of test strips**—Connect the burette containing the standard mixture (0.010 per cent by volume of carbon monoxide in air) to the apparatus and proceed as described for the blank. Discard the first determination and immediately perform a second and a third determination. Measure the length of coloration on both sides of the strip within 0.5 mm and take the average. Calibration is finished if the lengths of coloration on both sides are equal. Calibrate the test strips separately.

**Determination**—Transfer the air to be analysed (if necessary after dilution) to the burette and proceed as described above.

**Calculation**—The CO-content is calculated as per cent by volume (if the sample has not been diluted) using the formula  $0.01 l_b/l_y$  where  $l_b$  is the average length of the front and back side colorations in mm found by the determination, and  $l_y$  is the average length of the front and back side colorations in mm found by the calibration with 0.01 per cent by volume of CO in air.

**Note**—To ensure reproducibility of the results it is essential that the strips should be of uniform widths. The cutting device comprises a screw with a speed of 3.0 mm. A knife moving over lengths of 3.0 mm cuts strips of uniform widths.

During the preparation of mercuric oxide too long heating should be avoided to prevent pulverization.

The reaction tube is removed from the furnace whenever the apparatus is idle for more than five minutes. Thus fewer tests (i.e. fewer strips) are necessary to obtain a constant length of coloration.

The blank is only performed at the beginning of a series of determinations. If subsequent strips continue to reveal a coloration the mercuric oxide is reactivated by passing air at a rate of 10-12 litres hour at 250° C for one and a half hours.

It is most convenient to have a cylinder of standard gas (air containing 0.01 per cent by volume of carbon monoxide) available.

## COLORIMETRIC METHODS

Every strip of selenium sulphide reagent paper should be calibrated separately, because the different strips reveal some variance in selenium concentration and consequently in the length of the coloration. Calibration with one standard mixture (0.01 per cent CO) is sufficient because the length of the coloration is a linear function of the concentration.

The mercuric oxide should be activated : *a* when a mercuric oxide charge is replaced, *b* when the apparatus has been idle for a few days, *c* when the carbon filter has become inactive (aromatic compounds poison the mercuric oxide).

For *a* activation should be continued for three hours, whereas for *b* and *c* one and a half hours is sufficient.

The same test strip can be used for several determinations *e.g.*  $3 \times 50$  ml containing 0.002 per cent carbon monoxide gives the same length of black coloration as  $1 \times 50$  ml containing 0.006 per cent carbon monoxide.

After prolonged use the tube in which the reagent paper is inserted reveals a black precipitate of metallic selenium. This does not interfere and may be removed by heating over a flame while passing air through the apparatus. During this strong heating the tube containing mercuric oxide should be protected by asbestos.

### INDIRECT DETERMINATION OF CARBON MONOXIDE IN AIR WITH SELENIUM SULPHIDE

**Principle**—When the carbon monoxide present in the air to be analysed originates from coke oven gas, water gas *etc* a direct determination is impossible because the air then also contains hydrogen, which interferes, also producing a black coloration of selenium sulphide paper reagent. It is possible, however, to determine the carbon monoxide indirectly, but it is essential that the coke oven gas, water gas *etc* should vary little in composition ; the approximate carbon monoxide content of the sample should be known and the selenium sulphide reagent calibrated with coke oven gas, water gas *etc*.

**Procedure**—This is similar to the microdetermination of carbon monoxide in air by means of selenium sulphide paper (p 159).

**Calibration**—Calibrate the test strips with mixtures of air and coke oven gas or air and water gas or producer gas.

Take as standard mixture for coke oven gas a concentration of 0.10 per cent by volume in air and for other gases such a concentration that a coloration of 25-30 mm length is obtained.

**Calculation**—The carbon monoxide content is calculated in per cent by volume using the formula :  $l_b \times 0.10 \times x/100l_b$ , where  $l_b$  is the average length of the front and back side colorations in mm



found in the determination,  $l_y$  is the average length of front and back side colorations in mm found in the calibration with 0.10 per cent by volume of coke oven gas in air, and  $x$  is the per cent by volume of carbon monoxide in coke oven gas.

**Note**—After some 20 determinations with mixtures of coke oven gas and air the mercuric oxide should be reactivated at 250° C for about two hours while passing a stream of air at a rate of 10-12 litres/hour. The mercuric oxide must not come into contact with air mixtures containing 0.15 per cent or more of coke oven gas because such mixtures decrease the reactivity of the mercuric oxide excessively.

As a result of the interfering action of hydrogen, both the gas rate (50 ml in three minutes) and the reaction temperature (163° C  $\pm$  1°) should be kept constant within narrow limits.

If more than one apparatus is used each is calibrated separately. Owing to partial oxidation of hydrogen the length of coloration is dependent on contact time of the gas with mercuric oxide and the reactivity of mercuric oxide.

The reactivity is subject to fluctuations. It is wise to check after every reactivation whether a mixture of 0.10 per cent volume of coke oven gas produces the original length of coloration.

### CHLORINE

**Principle**—Chlorine reacts with *o*-tolidine producing a yellow colour.

#### REAGENTS

*o*-tolidine—1 gm *o*-tolidine of m.pt 130-131° C is dissolved in 100 ml hydrochloric acid, sp gr 1.19, and diluted with water to 1,000 ml.

**Standard**—A solution of 1 gm potassium dichromate in water is made up to 1 litre.

**Procedure**—Measure 10 ml of *o*-tolidine solution in the bubbler and draw the air through the reagent (1 stroke per 10 sec). Compare immediately in Nessler tubes with solutions containing 1, 2, 3 and 5 ml of potassium dichromate solution.

Table 22. Data for Chlorine Determination

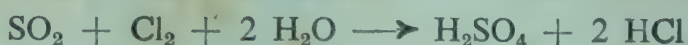
Potassium dichromate solution ml	5	3	2	1
No. of pump strokes	Volume of air $x$			
2	16,000	27,000	40,000	80,000
5	40,000	67,000	100,000	200,000
10	80,000	130,000	200,000	400,000
20	160,000	260,000	400,000	800,000
25	200,000	330,000	500,000	1,000,000



## HYDROGEN CYANIDE

**Result**—The result is expressed as 1 volume of chlorine in  $x$  volumes of air with the aid of Table 22.

**Note**—Nitrous fumes and sulphur dioxide interfere because of their reaction with chlorine :



## HYDROGEN CYANIDE

**Principle**—Hydrogen cyanide produces a stain on test paper prepared with benzidine and copper acetate or with congo red and silver nitrate.

### REAGENTS

**Benzidine-copper acetate**—Dissolve 2-3 gm benzidine acetate by shaking for 15 minutes with 100 ml water of 80° C. Cool and filter. The filtrate contains  $c$  1 per cent benzidine acetate and should not be kept longer than 2 days.

Dissolve 3 gm copper acetate in 100 ml water.

**Test paper**—Immerse a filter paper for 1 minute in a mixture of 25 ml of the benzidine solution and 2 ml of the copper acetate solution, drain and dry until moist and use immediately. The mixture of the two solutions should not be kept longer than 15 minutes.

**Congo red-silver nitrate**—Prepare a solution of 1 gm congo red in 100 ml water and dilute to 1 part in 20 with water.

Dissolve 5 gm silver nitrate in 100 ml water.

**Test paper**—Soak a filter paper for 1 minute in the congo red solution and dry. Then immerse it in the silver nitrate solution and dry away from strong light. Use immediately.

**Procedure**—Draw the air through the test paper clamped in the holder, and compare immediately with the standard. Repeat with a fresh test paper and a greater or smaller number of strokes of the pump.

**Note**—The moist benzidine-copper acetate test paper is protected by a strip of ordinary filter paper inserted in the holder behind the test paper.

The presence of chlorine, bromine, hydrochloric acid, hydrogen sulphide and sulphur dioxide, interferes with the benzidine-copper acetate test.

The congo red-silver nitrate test is affected by acid as well as by alkaline gases, and even by smoke.

## HYDROGEN SULPHIDE

**Principle**—Hydrogen sulphide produces a stain of lead sulphide on test paper impregnated with lead acetate.

### REAGENTS

The filter paper is immersed for 1 minute in a solution of 10 gm lead acetate in 100 ml water with 5 ml glacial acetic acid. The paper is drained and dried and stored in a stoppered bottle containing a drying agent. It should not be kept longer than a fortnight.

**Procedure**—The air is drawn slowly and regularly through the test paper clamped in the holder. Comparison is made with the standard within 10 minutes. The test is repeated with a fresh test paper and, according to the result of the first test, with a larger or smaller volume of the air.

## DETECTION AND DETERMINATION OF MERCURY IN AIR

**Colorimetrically**<sup>3</sup>—At a temperature of 70° C and a velocity of 1 m/sec the air is blown against a sheet of filter paper coated with a thin layer of selenium sulphide. From the depth of the black coloration, resulting from the formation of mercuric sulphide, and the volume of the air, the mercury content can be determined with the aid of a calibrated colour chart. The sensitivity of this method amounts to 1 in 10<sup>8</sup> parts by volume.

The selenium sulphide is prepared by passing hydrogen sulphide through a solution of 100 mg aluminium chloride per litre water, while a N solution of selenious acid is slowly added. The hydrogen sulphide should always be present in excess. The precipitate is filtered, washed, dried and stored away from the light. The selenium sulphide is spread over the filter paper by means of a plug of cotton.

**Photometrically**<sup>4</sup>—When the light of a low pressure mercury lamp falls on a screen and a dish containing some mercury is put between the lamp and the screen, the mercury vapour given off by the mercury in the dish shows as dark clouds on the screen. When the light transmitted by the lamp falls on a photoelectric cell the absorption of the light can be determined electrically as a measure of the concentration of the mercury vapour present in the space between the light source and the photoelectric cell.

The sensitivity amounts to 1 mg of mercury in 10 m<sup>3</sup> of air.

**By concentration**—The air is passed through a tube which is cooled in liquid nitrogen. At intervals chlorine is added to the air stream. A definite quantity of air is condensed and subsequently evaporated: this leaves a residue containing the mercury as mercuric chloride. The mercury is deposited by electrolysis on a copper electrode and transferred into a glass capillary tube by distillation.

## NITROUS FUMES

By centrifuging in alcohol the mercury is separated as a drop, the diameter of which is determined under a microscope. The mercury can also be dissolved and determined colorimetrically with dithizone.

Another method is to pass the air together with bromine vapour through water and to determine the mercury in the resultant solution of mercuric bromide with dithizone.

## NITROUS FUMES

**Principle**—Nitrous fumes produce a red colour with a solution containing 1-naphthylamine and sulphanilic acid.

### REAGENTS

*Acetic acid*—140 ml glacial acetic acid in 1,000 ml water.

*Sulphanilic acid*—500 mg dissolved in 150 ml acetic acid.

*Naphthylamine*—100 mg in 20 ml boiling water, poured into 150 ml acetic acid.

*Standard*—100 mg dimethylaminoazobenzene dissolved in and made up with acetone to 100 ml. 5 ml of this stock solution is diluted with acetone and made up to 250 ml. It must be kept in the dark.

**Procedure**—Measure 5 ml of sulphanilic acid solution and 5 ml of 1-naphthylamine solution into the bubbler and 1 ml of the standard solution into a tube of the same diameter. Make up the volume in this tube to 10.0 ml by adding 2 N hydrochloric acid. Connect the bubbler to the pump and draw the air slowly through the reagent (1 stroke per 10 sec) until the colour is a little less intense than that of the standard. Disconnect the bubbler and compare the colours after 2 minutes. Replace the bubbler if the colour is still less than the standard and make further strokes on the pump until equivalence is reached on standing for 2 minutes.

Table 23. Data for Nitrous Fumes Determination

<i>Volumes air x</i>	<i>No. of pump strokes</i>
8,000—13,000	1—2
13,000—20,000	2
20,000—27,000	3
27,000—35,000	4
35,000—45,000	5
45,000—55,000	6
55,000—65,000	7
65,000—75,000	8
75,000—85,000	9
85,000—100,000	10



**Result**—The result is expressed as 1 volume of nitrous fumes per  $x$  volumes of air with the aid of Table 23.

**Note**—The solution of the reagent should be colourless.

### SULPHUR DIOXIDE

**Principle**—Sulphur dioxide produces a blue stain on a test paper prepared with potassium iodate and starch.

#### REAGENT.

1 gm soluble starch is made into a paste with 10 ml 0.02 N barium hydroxide and added to a boiling solution of 1 gm potassium iodate and 2 gm potassium iodide in 50 ml 0.02 N barium hydroxide. The solution is cooled, shaken with 30 ml glycerol and diluted with distilled water to 100 ml.

The filter paper is immersed in the reagent for 30 seconds, drained, pressed between dry filter paper and dried at 50° C. The paper should be white and slightly moist and be used within a few hours. The solution should not be kept longer than 7 days.

**Procedure**—Clamp the test paper in the holder and draw the air slowly and steadily through (1 stroke per 3 sec). After three strokes the stain is compared with the standard chart. Repeat the test with a fresh test paper and a greater or smaller number of strokes.

**Note**—Other gases which reduce potassium iodate must be absent.

### ANILINE

**Principle**—The aniline vapour is absorbed in hydrochloric acid and oxidized by bleaching powder. The solution is made alkaline with ammonia and phenol is added. In the presence of traces of aniline the solution develops a deep blue colour.

#### REAGENTS

*Hydrochloric acid 1 per cent*—25 ml concentrated acid, specific gravity 1.19, is diluted with water to 1,000 ml.

*Bleaching powder*—5 gm bleaching powder, containing not less than 25 per cent available chlorine, is mixed with 100 ml water, heated to 50° C and filtered. The solution keeps one week.

*Phenol solution*—5 gm phenol is dissolved in 100 ml dilute aqueous ammonia, made from 50 ml concentrated ammonia, sp gr 0.880, diluted with water to 1,000 ml. The solution must not be kept for more than 3 days.

*Standard*—280 mg toluidine blue is dissolved in water and made up to 1,000 ml.

**Procedure**—Measure 10 ml of 1 per cent hydrochloric acid into the bubbler and draw the air through (1 stroke per 10 sec). Detach the

## BENZENE

bubbler after 5 strokes and transfer the contents to a test tube. Add 2 drops of bleaching powder solution, allow the mixture to stand for 5 minutes and heat to boiling. Add 5 ml of phenol solution and allow to stand for 15 minutes before transferring to a Nessler tube. Compare with Nessler tubes filled with the standard colours, prepared by making up 3.5, 7.0, 10.0, 15.0 and 20.0 ml of toluidine blue solution to 100 ml.

**Result**—The result is expressed as 1 volume of aniline vapour in  $x$  volumes of air, with the aid of Table 24.

**Note**—The depth of the colour of the standard solution may vary for different supplies of the dye. The standard containing 10.0 ml of toluidine blue in 100 ml should have exactly the same colour as a solution of 30 gm  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in water made up to 10 ml, to which is added 1.2 ml of a freshly prepared solution of 300 mg  $\text{KMnO}_4$  in 100 ml water. If any difference is observed the toluidine solution must be adjusted until an exact match is obtained.

Table 24. Data for Aniline Determination

No. of pump strokes	1	3	5	10
Volume of air $x$	Volume of standard solution ml			
5,000	10—15	—	—	—
10,000	7	15	—	—
15,000	—	10—15	20	—
20,000	3.5	10	15	—
30,000	—	7	10	20
50,000	—	—	7	10—15
100,000	—	—	3.5	7
200,000	—	—	—	3.5

## BENZENE

**Principle**—The air is bubbled through a solution of formaldehyde in sulphuric acid, which develops an orange-brown colour when the air contains benzene, toluene or coal tar naphtha.

### REAGENTS

**Test solution**—0.5 ml of 40 per cent formaldehyde is measured out into the bubbler and 10 ml of sulphuric acid (sp gr 1.84) is stirred in.

**Standard**—10 ml of a solution of sodium nitroprusside, made by dissolving 1 gm in distilled water made up to 100 ml, is measured into a tube of the same diameter as the bubbler.

**Procedure**—Connect the bubbler with the pump and draw the air through (1 stroke per 10 sec) until the solution in the bubbler has the same colour as the standard.

**Result**—The result is expressed in 1 volume of benzene per  $x$  volumes of air using Table 25.

**Note**—Thiophene and unsaturated hydrocarbons interfere with the test.

Table 25. Data for Benzene Determination

<i>Volumes air x</i>	<i>No. of pump strokes</i>
700—1,200	1—2
1,200—1,500	2
1,500—2,000	3
2,000—2,500	4
2,500—3,000	5
3,000—3,600	6
3,600—4,200	7
4,200—4,700	8
4,700—5,300	9
5,300—6,000	10
7,000	12
8,000	15
10,000	18

HUBBARD and SILVERMAN<sup>5</sup> describe a rapid method for determining benzene and its homologues in air by silica gel treated with sulphuric acid and formaldehyde. The sample is drawn through a narrow tube filled with the indicator gel. Aromatic hydrocarbons produce a stain, the length of which is proportional to the concentration and to the chemical reactivity of the aromatic hydrocarbons. The interference of other hydrocarbons and of water vapour is not significant.

## ORGANIC HALOGEN COMPOUNDS

**Principle**—A non-luminous flame, in contact with copper wire, burning in an atmosphere contaminated with an organic halogen compound is coloured green.

**Apparatus**—Alcohol blow lamp provided with a fine copper gauze.

**Procedure**—Fill the lamp three quarters full with pure alcohol, light it and adjust the flame. The flame should be non-luminous and colourless. Enter the atmosphere to be tested with the burning lamp and observe the colour of the flame against a dark background. Return the lamp to a room where the air is not contaminated, and allow the flame to burn until it is colourless. Extinguish the flame and release the pressure on the reservoir.



## ARSENIC

**Result**—The result is expressed as 1 volume of halogen compound in  $x$  volumes of air with the aid of Table 26.

**Note**—This test must not be carried out in the vicinity of inflammable liquids.

Table 26. Determination of Organic Halogen Compounds

Compound	Concentration : 1 vol. in $x$ vols. air		
	Flame Colour		
	Just visible	Pale Green	Bright Green
Dichlorethylene Dichlorethane	$x = 17,500$	12,500	10,000
Trichlorethylene Trichlorethane Tetrachlorethane	22,000	17,500	12,500
Pentachlorethane Perchlorethylene	25,000	20,000	15,000
Carbon tetrachloride	32,000	25,000	16,000
Monochlorobenzene	10,000	7,000	4,500
Methyl bromide	30,000	15,000	10,000—5,000

## DETECTION AND DETERMINATION OF TOXIC SUBSTANCES IN SOLUTION

### ARSENIC

**Principle**—The material is treated with tin and hydrochloric acid. The arsenic is reduced to arsine. The hydrogen carrying the arsine is passed over a heated quartz coil, where the arsine is decomposed and the arsenic deposited. The arsenic mirror is dissolved in iodine monochloride, liberating an equivalent amount of iodine which is titrated with potassium iodate and concentrated hydrochloric acid.



**Apparatus**—The apparatus is illustrated in Figure 37.

#### REAGENTS

**Hydrochloric acid**—Sp gr 1.19 free from arsenic.

**Finely divided tin**—Prepared by reducing tin chloride with arsenic-free tin and hydrochloric acid.

**Hydrogen**

**Iodine monochloride solution**—Prepared by dissolving 1.56 gm potassium iodide and 1 gm potassium iodate in 50 ml water ; adding 50 ml hydrochloric acid sp gr 1.19, and removing the separated

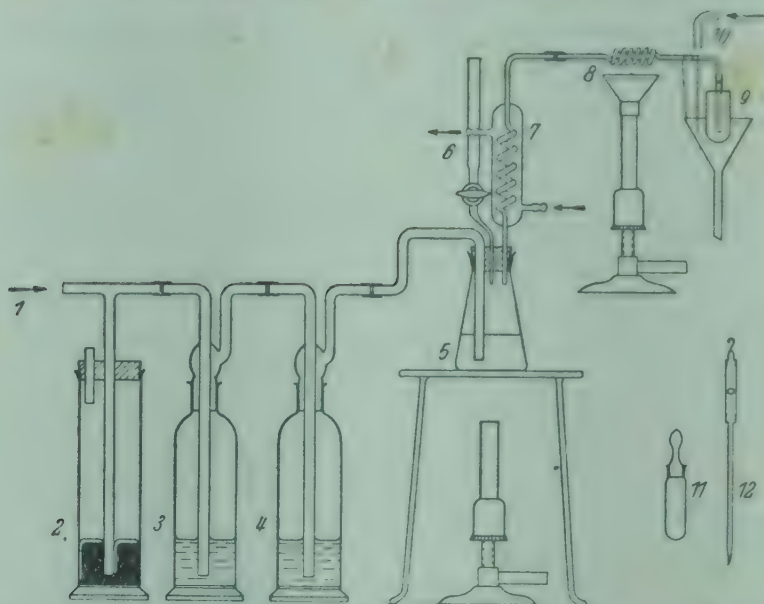


Figure 37. Apparatus for iodimetric determination of small amounts of arsenic : 1 hydrogen inlet, 2 mercury filled pressure regulator and safety valve, 3 wash bottle with  $\text{KMnO}_4$ , 4 wash bottle with  $4N \text{ H}_2\text{SO}_4$ , 5 100 ml conical flask containing Sn, 6 funnel, 7 condenser, 8 quartz coil, 9 bubble counter, 10 cooling water supply, 11 10 ml test tube with ground glass stopper, 12 2 ml pipette with tip drawn out.

iodine by adding a few drops of carbon tetrachloride and then sufficient dilute potassium iodate solution until the carbon tetrachloride is colourless. The solution should be kept away from the light.

#### *Carbon tetrachloride*

*Potassium iodate solution*—Containing  $1 \mu\text{g-mol KIO}_3$  per gm of solution.

**Sample**—The solution to be analysed should contain 20-50, preferably  $30 \mu\text{g}$  trivalent arsenic.

**Procedure**—Transfer into the conical flask 10 ml hydrochloric acid and 20 gm finely divided tin. Pass hydrogen through the apparatus for ten minutes. Connect up the quartz coil and pass hydrogen for another two minutes. Heat the coil to redness, taking care that no water condenses behind it. Adjust the velocity of the stream of hydrogen to one bubble per second.

Transfer the sample through the funnel into the conical flask. Wash the funnel with hydrochloric acid until the tin in the conical flask is just covered.

Turn on the cooling water and heat the flask gently so that the boiling point is reached in approximately thirty minutes. Allow the liquid to boil gently for an hour, taking care to provide adequate

## COLORIMETRIC DETERMINATION OF TRACES OF COPPER

cooling in order to prevent the water vapour from condensing behind the heated coil. Allow the coil to cool and disconnect from the apparatus.

Add 0.3 ml of iodine monochloride solution to the test tube. Draw this liquid into the coil so that the arsenic mirror is dissolved. Allow the liquid to flow back into the test tube and wash the coil with 1 ml hydrochloric acid and 1 ml water. Add 2 drops of carbon tetrachloride and allow the tube to stand for fifteen minutes away from the light.

Weigh the pipette filled with potassium iodate solution to within 1 mg. Titrate the iodine separated in the test tube slowly, shaking continuously with the potassium iodate solution until the purple colour of the carbon tetrachloride has just disappeared. Weigh the pipette again within 1 mg. Perform a blank in the same way.

**Results**—The amount of arsenic  $p$   $\mu\text{g}$  present in the sample is calculated using the formula :  $p = 60 (g_1 - g_0) t$  where  $g_1$  is weight in gm of potassium iodate solution consumed in the test,  $g_0$  is the weight in gm of this solution consumed in the blank, and  $t$  is the quantity of  $\text{KIO}_3$  in  $\mu\text{g-mol}$  per gm of potassium iodate solution.

The results are expressed within 1  $\mu\text{g}$ .

**Note**—Condensation of water vapour in the coil prevents quantitative deposition of arsenic.

At the end of the titration the concentration of the hydrochloric acid should not be lower than 1 volume of hydrochloric acid in 2 volumes of water, otherwise the reaction of potassium iodate with iodine is no longer quantitative.

The titration should be performed in daylight. In artificial light the colour change is difficult to observe. The point of the pipette should be drawn out to such a length that 1 drop weighs 3.5 mg. If the tin contains so much arsenic that the blank has a high value, it should be boiled for a few hours with hydrochloric acid while hydrogen is passed through it.

## COLORIMETRIC DETERMINATION OF TRACES OF COPPER IN AQUEOUS SOLUTION USING DITHIZONE

**Principle**—Cupric ions react with dithizone (diphenylthiocarbazone) to form a violet complex compound, slightly soluble in water and readily soluble in carbon tetrachloride, so that it can be concentrated by shaking the aqueous solution with a small volume of carbon tetrachloride. The concentration of the complex is determined colorimetrically.

A great many other cations form coloured compounds with dithizone, which however unlike the copper complex are unstable in



dilute acid, so that copper can be determined in the presence of practically all other metals.

Trivalent iron interferes with the determination because it oxidizes the dithizone. It is rendered harmless by reduction with hydroxylamine.

**Apparatus**—Separating funnel, 100 ml.

#### REAGENTS

*Hydroxylamine solution*—100 gm/litre

*Thymol blue*—0.4 gm/litre in 96 per cent alcohol

*N sulphuric acid*

*Dithizone solution*—Dissolve 10 mg dithizone in 100 ml carbon tetrachloride, filter and shake the filtrate in a separating funnel with 100 ml 0.1 N ammonia, in which the dithizone is dissolved. Wash the solution twice with a small amount of carbon tetrachloride removing the latter after each washing. Then add 250 ml of carbon tetrachloride and acidify with sulphuric acid. Shake until the pure dithizone set free from the ammoniacal solution has entirely passed into the carbon tetrachloride layer. Finally wash the dithizone solution with distilled water until all acid has been removed.

*Distilled water*—twice distilled in a glass apparatus

*Copper sulphate*—solution containing 1 mg copper per litre

*Buffer solution*—pH 2.2 : 0.1 N potassium diphthalate and 40.7 ml of 0.1 N HCl per litre.

**Sample**—The sample should not contain more than 10  $\mu$ g copper.

**Procedure**—Transfer the sample into a separating funnel and add a small excess of hydroxylamine solution so that the iron is completely reduced. Neutralize the solution with sulphuric acid, using thymol blue as the indicator (pH about 2) and add 5 ml of the buffer solution. Add 5 ml of the dithizone solution and shake for five minutes. If the red coloration is deep, add more dithizone solution. If the colour remains dark, dilute the solution with carbon tetrachloride.

Transfer a volume of distilled water, equal to the volume of the sample, into a second separating funnel. Add the same amount of reagents as before. Titrate the liquid with copper sulphate solution with constant shaking until the layer of carbon tetrachloride shows the same coloration as that in the sample.

**Results**—The copper content  $p$  of the water is calculated in mg per litre using the formula  $p = vt/V$  where  $V$  is the volume in ml of sample treated,  $v$  is the volume in ml of copper sulphate solution, and  $t$  is the titre of the copper sulphate solution in mg per litre.

**Note**—To remove heavy metals the glassware and the reagents should be shaken with dithizone solution until the latter keeps its green colour.

## DETERMINATION OF FLUORINE IN FLUORIDES

Any undissolved residues which must be considered as part of the sample should be dissolved by the addition of acid.

### DETERMINATION OF FLUORINE IN FLUORIDES

**Principle**—After phosphoric acid has been added the hydrofluoric acid is distilled and the hydrofluosilicic acid in the filtrate is titrated with thorium nitrate, using alizarine sulphonate as indicator.

**Apparatus**—The apparatus is shown in Figure 38.

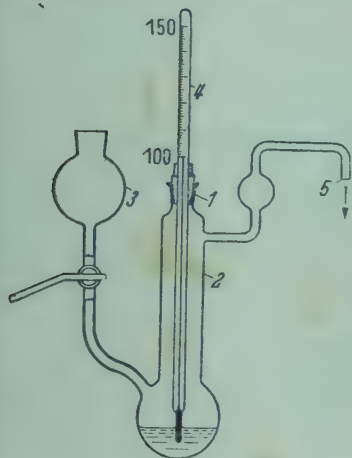


Figure 38. Apparatus for the determination of fluorine in fluorides : 1 ground glass fitting, 2 flask (length 230 cm, neck diam 35 cm, bulb diam 70 cm), 3 water reservoir (150 ml capacity, diam 60 cm), 4 thermometer for temperatures to 750° C, 5 connection to cooler.

#### REAGENT

**Indicator**—Sodium alizarine sulphonate containing 100 mg in 100 ml water

**Buffer solution**—94.48 gm monochloroacetic acid and 20 gm sodium hydroxide per litre

**0.08 N thorium nitrate**—11.0444 gm  $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$  per litre

**Phosphoric acid**—sp gr 1.70

**N Sodium hydroxide solution**

**0.1 N Hydrochloric acid solution.**

**Sample**—The amount of the sample taken for the analysis should not contain more than 20 mg fluorine to prevent the precipitation of thorium fluoride which interferes. Nitrate ions do not interfere.

**Procedure**—Transfer the sample to the distillation flask and add 15 ml phosphoric acid and pumice. Distil at 130-135° C and collect 150 ml distillate in a 250 ml measuring flask. Make up the volume of the distillate to 250 ml, mix and transfer 100 ml to a conical flask. Add 3 drops of the indicator, add a slight excess of sodium hydroxide solution and neutralize with hydrochloric acid.

Add 5 ml of the buffer solution and titrate with thorium nitrate until the colour just turns pink. Titrate drop by drop while shaking continuously.

**Results**—Calculate the fluorine content with the aid of the graph.

**Note**—The graph is based on analyses of samples containing known amounts of fluoride.

## DETERMINATION OF SEMI-MICRO AMOUNTS OF MERCURY

**Principle**—The inorganic mercury solution is reduced with stannous chloride, the mercury collected, dissolved in nitric acid and titrated with thiocyanate.

### REAGENTS

*Ferric alum indicator*—400 gm of ferric alum is dissolved in water, acidified with nitric acid, and made up to 1 litre.

*Standard mercuric nitrate*—The appropriate amount of mercury is dissolved in concentrated nitric acid, oxides of nitrogen and mercurous ions are oxidized by adding potassium permanganate solution. The excess permanganate is destroyed with ferrous sulphate solution and the mercury solution is diluted with water to the desired volume.

*Standard potassium thiocyanate*—A solution of the recrystallized salt is prepared and standardized against the standard mercury solution, using ferric alum as indicator.

*Ferrous sulphate*—100 gm  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is dissolved in 0.5 N sulphuric acid and made up with water to 1 litre.

*Stannous chloride*—500 gm  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is dissolved in 300 ml concentrated hydrochloric acid and made up with water to 1 litre. The solution is heated with metallic tin until clear and stored over tin.

*Potassium permanganate*—A saturated solution is prepared and decanted after standing for several days.

**Sample**—The sample should be a solution preferably containing 3-10 mg mercury per ml.

**Procedure**—Transfer 10 ml of sample into a centrifuge tube and add a few drops of hydrochloric acid sp gr 1.19. Heat to  $50^\circ \text{C}$ , add a mixture of 3 ml hydrochloric acid and 3 ml stannous chloride heated to the same temperature. Allow the precipitate to stand for five minutes reheat to  $50^\circ \text{C}$  and centrifuge for five minutes at 1,500 r.p.m. Repeat this operation if all the mercury has not collected in globular form.

Remove the supernatant liquid by means of a fine porous glass immersion filter. Wash the precipitate 2-3 times with 2 ml portions of 2 N sulphuric acid and then with water till the wash water is free of chloride ions. Place the immersion filter in the centrifuge tube, add 2 ml concentrated nitric acid and allow to stand until the



## DETERMINATION OF MERCURY IN BIOLOGICAL MATERIAL

mercury is dissolved. Transfer the solution to a 125 ml conical flask. Insert the filter in a rubber stopper provided with a bent glass tube and fitting in the conical flask. Wash the filter with water, applying suction. Remove the stopper, add potassium permanganate drop by drop to slight excess, destroy the excess with a drop of ferrous sulphate, dilute the solution to 30 ml and titrate with potassium thiocyanate at 12-13° C using 3-4 ml of indicator.

**Note**—Mercury in organic compounds can be determined by dissolving the sample in dioxane and subsequently reducing it with the stannous chloride and hydrochloric acid.

## DETERMINATION OF MERCURY IN BIOLOGICAL MATERIAL

**Principle**—The material is digested with sulphuric acid, mercury is distilled off as chloride and the mercury in the distillate determined with dithizone (diphenylthiocarbazone). Copper dithizonate is removed by treating the dithiazonate extract with ammonia.

### REAGENTS

*Dithizone*—50 mg of diphenylthiocarbazone is dissolved in a litre of redistilled carbon tetrachloride.

*Sulphuric acid* sp gr 1.84

9 N ammonia

Chlorine

**Apparatus**—This comprises a Kjeldahl flask with a ground in funnel and receiver as shown in Figure 39.

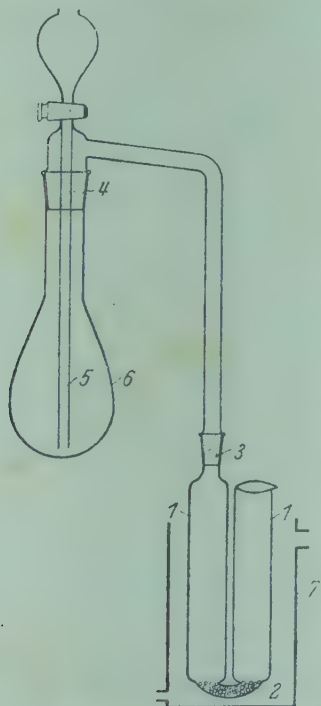


Figure 39. Apparatus for determination of mercury in biological material according to KOSLKA : 1 4 cm × 20 cm test tubes, 2 glass beads, 3 14/15 ground glass joint, 4 34/35 ground glass joint, 5 1 cm diam tube, 6 800 ml Kjeldahl flask, 7 water bath.

**Procedure**—Introduce 25 gm of the sample into the Kjeldahl flask, and add glass beads, 1.0 gm copper sulphate and 15-20 gm ammonium sulphate. Close the flask and add sulphuric acid through the funnel using 50 ml for blood or 75 ml for other tissues.

After digestion is completed pass chlorine gas through the digest while heating for twenty minutes with a medium sized flame. Remove the chlorine tube and aspirate air through the apparatus and the distillate to remove the excess chlorine.

Transfer the distillate to a separating funnel and bubble sulphur dioxide through the solution to decompose the hypochlorous acid completely. Neutralize with ammonia until thymol blue just changes from red to yellow. Cool the solution in running water, add 25.0 ml dithiazone and shake for a minute. Wash the carbon tetrachloride containing the mercury dithizonate twice with 50 ml 9 N ammonia and drain off the carbon tetrachloride layer. Filter into a colorimeter tube and determine the concentration photometrically or by comparing with a standard.

**Detection and determination in organic material**—After the destruction of the organic material by nitric and sulphuric acids and potassium chlorate, a solution is obtained from which, after the addition of cadmium chloride, the mercury together with cadmium sulphide is precipitated by hydrogen sulphide. The sulphides are dissolved. The flattened end of a copper wire, moistened with the solution, is put into contact with paper treated with an ammoniacal silver solution. If the solution contains mercury a brown spot is formed. In this case, the solution of sulphides is reduced with alkaline formaldehyde. The mercury is separated with a precipitate of barium sulphate in which it is determined iodometrically, nephelometrically, by the reaction with Nessler's reagent, or colorimetrically.

## COLORIMETRIC DETERMINATION OF NITRATE WITH SODIUM SALICYLATE

**Principle**—The reaction of the nitrate with salicylic acid and sulphuric acid produces a nitrocompound. After addition of sodium hydroxide solution in excess the yellow colour of the nitrocompound is compared with that of standard solutions.

**Apparatus**—Porcelain dishes, diameter approx 7 cm, and colorimeter tubes, 50 ml.

### REAGENTS

Sodium salicylate solution, 5 gm sodium salicylate, 50 ml sodium hydroxide (1N) and 950 ml water

Sodium chloride solution 20 gm/litre

Sulphuric acid (sp gr 1.84)

## COLORIMETRIC DETERMINATION OF TRACES OF ZINC

**Sodium hydroxide, 4N**

Standard nitrate solution containing 0.163 gm potassium nitrate per litre. 1 ml corresponds to 0.1 mg  $\text{NO}_3$

Dilute standard. For the colorimetric determination this solution is diluted 1 to 9.

**Sample**—Take for each determination 25 ml of the solution of the nitrate in water containing approx 0.1 mg  $\text{NO}_3$ .

**Procedure**—Transfer the sample to a porcelain dish. Add 5 drops sodium chloride solution and 1 ml sodium salicylate solution and evaporate on the water bath.

Moisten the residue after cooling with 1 ml sulphuric acid and allow to react for exactly 10 minutes. Transfer the contents of the dish quantitatively to a colorimeter tube, add 10 ml sodium hydroxide and make up with water.

Compare with solutions obtained in the same way, starting with respectively 8, 9, 10, 11 and 12 ml dilute standard.

**Results**—Calculate the  $\text{NO}_3$ —content of the sample ( $p$ ) in mg/l with the formula :

$$p = \frac{1,000}{V}$$

where  $a$  = mg  $\text{NO}_3$  of the corresponding standard solution

$V$  = ml sample taken for the analysis.

## COLORIMETRIC DETERMINATION OF TRACES OF ZINC IN AQUEOUS SOLUTION WITH DITHIZONE

**Principle**—Zinc reacts with dithizone (diphenylthiocarbazone) to form a red complex compound which is slightly soluble in water and readily soluble in carbon tetrachloride so that by shaking with carbon tetrachloride the compound can be extracted from a large volume of water and determined colorimetrically in the carbon tetrachloride solution.

Many other metals also react with dithizone to give coloured compounds but the formation of these compounds can be inhibited by the addition of sodium thiosulphate. The action of thiosulphate depends upon the pH of the solution. If the pH exceeds 5.5 the inhibitory action is insufficient and results are too high. If the pH is below 4.5 the formation of the zinc compound is also inhibited and the shaking must be continued a long time. The correct pH value, c 5, is obtained by means of a buffer mixture of sodium acetate and acetic acid.

Ferric ions interfere because they oxidize the dithizone. They are eliminated by adding Seignette salt.



**Apparatus**—Separating funnel, 100 ml.

#### REAGENTS

*Seignette salt*—Solution containing 100 gm of sodium potassium tartrate per litre

*Sodium thiosulphate*—Solution containing 200 gm per litre

*Bromcresolpurple*—Solution containing 0.1 gm per litre

*N Sulphuric acid*

*Buffer (pH 5.0)*—12 gm acetic acid and 27 gm sodium acetate dissolved in a litre of water.

*Dithizone*—See reagents for determination of copper, page 174

*Distilled water*—Distilled twice in a glass apparatus

*Zinc sulphate*—Solution standardized, containing *c* 1 mg zinc per litre.

**Sample**—Transfer *V* ml of the sample to a separating funnel and add Seignette salt until the iron is completely bound. Then add 10 ml sodium thiosulphate solution and neutralize with sulphuric acid using bromcresolpurple as indicator.

Add 10 ml buffer solution and 5 ml dithizone solution and shake for five minutes. If the colour turns red add more dithizone ; if the solution retains a dark colour, dilute with carbon tetrachloride.

Transfer to a second separating funnel *V* ml distilled water and equal quantities of reagents as in the first shaking and determination, titrate this liquid with zinc sulphate until with continuous shaking the layer of carbon tetrachloride acquires the same colour as that of the sample.

**Results**—The zinc content *p* of the sample is calculated by means of the formula :  $p = vt/V$  where *V* is the volume in ml of the sample taken for the determination, *v* is the volume in ml of the zinc sulphate consumed, and *t* the titre of the zinc solution in mg zinc per litre.

**Note**—In order to eliminate heavy metals the glassware and reagents should be taken with dithizone until the latter retains its green colour. Any undissolved parts which must be considered as part of the sample should be dissolved by the addition of acid.

## DETECTION AND DETERMINATION OF TOXIC SUBSTANCES IN BREATH, BLOOD AND URINE

### DETECTION OF ALCOHOL IN EXHALED AIR

**Principle**—The exhaled air collected in a rubber bulb is passed through an alkaline solution of potassium permanganate. The alcohol is oxidized to acetic acid.



## DETECTION OF ALCOHOL IN EXHALED AIR

The permanganate is reduced to manganate which has a green colour. The reaction proceeds rapidly in the presence of a considerable excess of permanganate and at a high alkalinity. The depth of the green coloration is measured photometrically at a wavelength for which the absorption of this colour is maximal. The extinction coefficient of the solution is a measure for the amount of alcohol oxidized by the solution.

### REAGENTS

0.100 N *potassium permanganate solution*

4 N *sodium hydroxide solution*

**Apparatus**—The apparatus is illustrated in Figure 40.

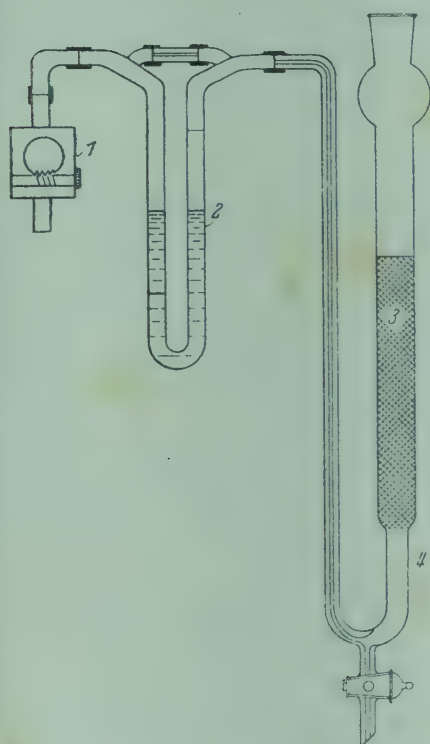


Figure 40. Apparatus for determination of alcohol in exhaled air : 1 gas regulator, 2 flowmeter containing water, 3 absorption vessel containing alkaline  $\text{KMnO}_4$  solution and 5 mm diam glass beads, 4 tube in which the colour of the solution is observed.

**Sample**—The sample is obtained by inflating an entirely deflated rubber bulb.

**Procedure**—Measure in turn 4 ml potassium permanganate solution and 5 ml of sodium hydroxide solution into the absorption vessel 3. Connect the rubber bulb to the inlet of the gas regulator 1 and pass the air through the solution for exactly ten minutes at a rate of 12 litres/hour. Finally transfer the solution to a cuvette and determine the extinction coefficient with a photometer at a wavelength of  $600\text{m}\mu$  and a thickness of layer of 1 mm.

**Results**—The amount of alcohol  $p$  mg, present in 2 litres of exhaled air is found from the formula :

$$p = \frac{E - 2.35}{17.4}$$

where  $E$  is the extinction coefficient of the solution and 2.35 is that of the blank.

**Note**—From the alcohol content of the exhaled air  $p$  expressed as mg in 2 litres exhaled air, measured after  $t$  hours, the total alcohol consumption may be determined by means of the formula :

$$a = (p - 0.121 + t \times 0.044) 3.0 \times 10^5$$

where  $t$  is the number of hours elapsed between the moment when the first amount of alcohol was consumed and the moment of sampling.

The exhaled air should not be sampled sooner than one hour after the last amount of alcohol has been consumed.

The tube 3 containing the glass beads must be flushed twice with water before transferring the solutions to it.

## COLORIMETRICAL DETERMINATION OF ALCOHOL IN EXHALED AIR

**Principle**—The exhaled air is passed through an alkaline solution of potassium permanganate. In the presence of increasing amounts of alcohol the permanganate is progressively reduced to manganate, the colour of the solution changing from purple through blue into green. The colour of the solution which is a function of the amount of alcohol in the exhaled air is determined with the aid of standard colours.

### REAGENTS

0.020 N *potassium permanganate in N sulphuric acid*

10 N *sodium hydroxide*

*Standard solutions* numbered 1, 2, 3 and 4.

**Apparatus**—This is illustrated in Figure 40 on page 181.

**Sample**—The sample is obtained by inflating an entirely deflated rubber bladder.

**Procedure**—Measure in turn 5 ml of potassium permanganate solution and 5 ml sodium hydroxide solution into 3 by means of a pipette. Close the gas regulator, connect with the rubber bulb and pass the exhaled air through 3 for exactly five minutes at a rate of 12 litres/hour. Adjust the supply by means of the gas regulator 1 in such a manner that in either of the two limbs of the flowmeter 2 the surface of the liquid is kept at the level observed when passing 12 litres of gas per hour through it.



## DETECTION OF ALCOHOL IN BLOOD

Close the regulator / slowly so that the solution passes into 4. Compare the colour of the solution in 4 with the standard colours within one minute.

**Results**—The amount of alcohol in the exhaled air expressed in mg per litre is equal to the alcohol equivalent of the corresponding standard solution.

**Note**—Tube 3 containing the glass beads should be flushed twice with water before use. Traces of dirt or grease introduced into the apparatus produce the same reaction as alcohol. Clean the rubber bladder by inflating it repeatedly with pure air or with carbon dioxide. A blank should be performed daily with alcohol-free air in order to check the purity of apparatus and reagents. The reagent solutions must not be allowed to come in contact with the rubber bladders or the pipettes.

## DETECTION OF ALCOHOL IN BLOOD

**Principle**—The alcohol contained in the sample is swept out by a current of air and subsequently absorbed in dichromate and sulphuric acid. The excess dichromate is determined iodometrically. The quantity of dichromate used is a measure of the amount of alcohol in the blood.

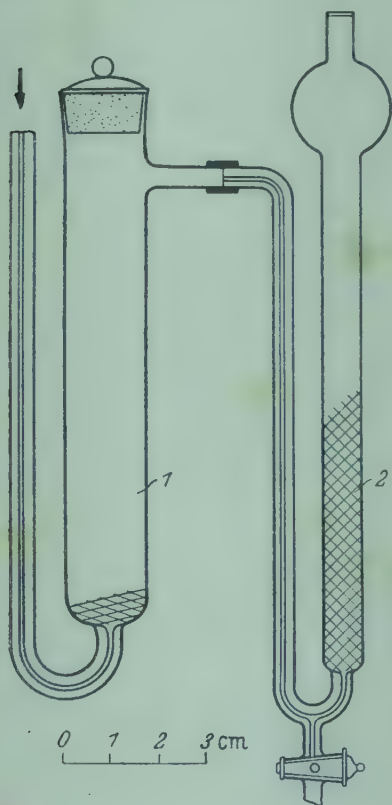


Figure 41. Apparatus for determination of alcohol in blood : 1 tube with ground glass stopper containing glass beads, 2 absorption vessel containing acidified dichromate solution and glass beads.

## REAGENTS

*Sodium thiosulphate solution*—Standardized, approximately 0.02 N.

*Potassium dichromate/sulphuric acid mixture*—5 gm potassium dichromate ( $K_2Cr_2O_7$ ) are dissolved in the minimum quantity of water and the volume made up to 1 litre with sulphuric acid, sp gr 1.84.

*Potassium iodide solution*—Containing 100 gm KI per litre.

*Calcium stearate suspension*—Containing 6.5 gm in 100 ml paraffin oil.

*Starch solution*—Containing 10 gm per litre.

**Apparatus**—The apparatus is illustrated in Figure 41.

**Sample**—About 1 gm oxalated blood is used as sample.

**Procedure**—Add 2 drops of calcium stearate suspension to the sample, transfer to the tube 1 and measure 2 ml dichromate sulphuric acid mixture into 2. Heat the tube 1 to about 70° C while passing a moderate stream of air through it. Continue passing the air for another thirty minutes. Then transfer the dichromate-sulphuric acid solution to a conical flask with ground stopper and wash out the absorption vessel five times with 5 ml water. Add 50 ml water and 10 ml potassium iodide solution. Allow the liquid to stand for a few minutes and titrate the iodine with standard thiosulphate solution using the starch solution as indicator.

**Blank**—Measure 2 ml dichromate sulphuric acid mixture with the same pipette into a conical flask, add 75 ml water and 10 ml potassium iodide solution and titrate with standard thiosulphate solution.

**Result**—The amount of alcohol in mg/gm of blood is calculated from the formula :

$$\frac{(V_0 - V) t \times 11.3}{p} = 0.07$$

where  $V_0$  is the volume in ml of thiosulphate solution consumed in the blood,  $V$  is the volume in ml of thiosulphate solution consumed in the test,  $t$  is the titre of the thiosulphate solution, and  $p$  the weight of sample in gm.

**Note**—The quantity of the sulphuric acid dichromate solution can also be weighed by means of a weight pipette. In order to calculate the quantity of blood present in the sample the ratio between the amounts of blood and oxalate solution in the sample must be known.

The hypodermic needle used for collecting the sample should not be sterilized with alcohol, ether or other oxidizable substances.

The calcium stearate is added to prevent foaming.

## URINE SULPHATE TEST (BENZENE)

**Introduction**—The ratio of inorganic sulphates to total sulphate in the urine may be used as a warning of chronic benzene poisoning.

## BENZENE IN BLOOD

It is a measure of the amount of benzene vapour breathed in the period immediately prior to the test. Low ratios indicate a harmful condition.

**Principle**—The inorganic sulphate is determined by precipitation as barium sulphate in the cold. The total sulphate is determined after boiling the acidified sample for thirty minutes.

### REAGENTS

*Hydrochloric acid (2 + 3)*

*N Barium chloride solution*

*2 N Sodium chloride solution*

**Procedure—Inorganic sulphate determination.** Measure 25 ml of the urine into a beaker and add 100 ml water, followed by 10 ml sodium chloride solution and 5 ml hydrochloric acid. Slowly add 10 ml of barium chloride solution. Filter after several hours and determine the weight of the precipitate.

**Total sulphate determination**—Measure into a beaker 25 ml urine. Add 10 ml of sodium chloride solution and 10 ml hydrochloric acid. Cover the beaker with a watch glass and boil the contents gently for thirty minutes, cool in running water and dilute with 100 ml water. Slowly add 10 ml barium chloride solution and filter after several hours. Determine the weight of the precipitate.

## BENZENE IN BLOOD

**Principle**—The benzene is expelled from a measured quantity of the sample by a stream of air and trapped in a mixture of sulphuric acid and nitric acid by which it is transformed to *m*-dinitrobenzene, which is determined colorimetrically. The sensitivity is 0.001 mg benzene.

**Apparatus**—The apparatus is shown in Figure 42.

### REAGENTS

*Red litmus paper*

**Nitrating acid**—A mixture of equal parts sulphuric acid, sp gr 1.84 and nitric acid sp gr 1.52

*N sodium hydroxide solution*

*Butanone*

**Calcium stearate**—1.3 gm suspended in 20 ml medicinal paraffin oil.  
**Solution of 17 gm sodium nitrate and 8.6 gm sodium sulphate in 1 litre of water.**

**Standard**—*m*-dinitrobenzene solution made by dissolving 108 mg of the substance in and making up to 100 ml with nitrating acid; 1 ml solution contains 0.5 mg benzene. A more dilute solution containing 0.05 mg benzene is made up by diluting 10 ml of the first solution to 100 ml with nitrating acid.



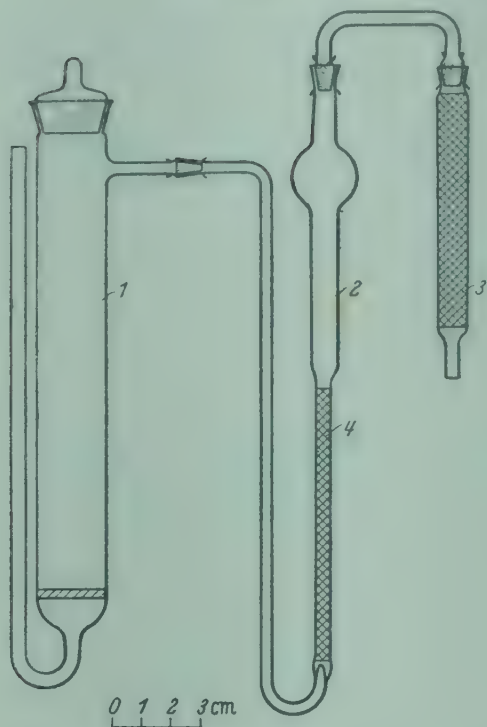


Figure 42. Apparatus for determination of benzene in blood : 1 tube fitted with sintered glass filter, 2 absorption tube containing  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , 1 + 1, 3 tube filled with solid  $\text{NaOH}$ , 4 tube filled with glass beads.

**Procedure**—Measure 5 or 10 ml sample in 1 (Figure 42) and mix with 0.5 ml calcium stearate. Measure 2 ml nitrating acid into the tube 2. Adjust the stream of air to flow at 3 litres per hour and pass 10 l of air through the apparatus. Shut off the air and allow the apparatus to stand for thirty minutes.

Disconnect the tube 2 and transfer its contents to a 100 ml measuring flask, washing five times with 1 ml portions of water. Measure known quantities of the dilute standard solution into 100 ml measuring flasks and add nitrating acid to make the volume in each up to 2 ml.

Neutralize the contents of the measuring flasks with sodium hydroxide while cooling them in running water and add one drop of sodium hydroxide in excess.

Heat the solution to  $30^\circ \text{C}$ , add 30 ml butanone to each flask, shake for ten minutes and transfer the liquid to separating funnels. Transfer the butanone layers into 15 ml cylinders with ground stoppers, add to each 1.5 ml sodium hydroxide solution, shake and keep in a dark place and compare the colours after one hour.

**Note**—The calcium stearate is added to prevent foaming.

#### COLORIMETRIC DETERMINATION OF CARBON MONOXIDE IN BLOOD WITH TANNIN

**Principle**—When tannin is added to blood diluted with water the tannin forms a typically coloured product with carbon monoxide-

haemoglobin. The colour is compared with standards prepared with samples of blood of a known carbon monoxide content treated in a similar manner. They are obtained by mixing blood free from carbon monoxide with blood saturated with it. The same reaction is shown by oxyhaemoglobin which however can be reduced to haemoglobin by adding pyrogallol.

**Apparatus**—Stoppered bottle (50 ml) ; pipettes of 2 ml ; measuring flasks of 20 ml ; burettes of 10 ml ; test tubes, length 8 cm, diameter 8 mm ; pipettes of 1 ml.

## REAGENTS

*Blood* (at least 5 ml) free from carbon monoxide.

*Tannin solution* containing 1 gm tannin and 1 gm pyrogallol in 50 ml water.

*Coal gas* which provides a convenient source of carbon monoxide (5-10 per cent).

**Sample**—A sample of at least 2.5 ml of blood should be available. In order to prevent coagulation of the blood, 10 mg potassium citrate should be added.

**Procedure**—Measure 2 ml of CO-free blood into a stoppered bottle and saturate with carbon monoxide by passing coal gas through the bottle until the air has been expelled. Close the bottle and shake for ten minutes. Transfer the blood quantitatively into a 20 ml measuring flask and dilute with water. Transfer 2 ml of CO-free blood and 2 ml of the CO-saturated blood into 20 ml measuring flasks and make up the volume with water. Shake and prepare standard solutions according to Table 27.

Table 27. Standard Solutions of Blood with and without CO

<i>CO-free blood ml</i>	<i>Blood saturated with CO ml</i>	<i>Saturation per cent</i>
4.5	0.5	10
4.0	1.0	20
3.5	1.5	30
3.0	2.0	40
2.5	2.5	50

Prepare a solution of the sample using 2 ml made up to 20 ml.

Transfer into each of the test tubes 1 ml of each of the standard solutions and of the diluted sample. Add 1 ml of reagent to each test tube, shake the contents and allow to stand for 30 minutes. Compare the colours.

**Results**—The result should be given within 5 per cent.

**Note**—The reagent should be prepared daily.

When sealed and stored in a cool place the test tubes with the standard solutions can be kept for a fortnight.

The CO-free blood should be human or bovine.

#### DETERMINATION OF CARBON MONOXIDE IN BLOOD BY THE LEIFO PHOTOMETER

**Principle**—After shaking the sample with air the extinctions of the oxalate blood, haemolysed with saponin, are determined at 578 and 546m $\mu$ . By means of a graph the carbon monoxide content of the blood is calculated from the quotient of the two extinctions  $E_{578}$  and  $E_{546}$ .

**Sample**—The haemolysed oxalate blood is prepared as follows : Approximately 1 ml blood obtained by puncture is transferred to a test tube containing two drops of a saturated sodium oxalate solution, 2 ml of saponin solution and a layer of toluene. The point of the syringe is immersed in the saponin solution.

**Procedure**—Transfer five drops of the haemolysed sample into the micro-cuvette with a pipette. Stir for ten seconds with a glass rod, close the cuvette, adjust the depth of the solution to 0.3–0.5 mm and insert the cuvette into the photometer. Determine extinction coefficients for 578 and 546m $\mu$ .

**Calculation**—The quotient  $R$  of the extinction coefficients is found from  $R = E_{578}/E_{546}$ .

The percentage of carboxy-haemoglobin is read from the graph.

#### ESTIMATION OF DUST \*

The estimation of dust should include not only the concentration but also the particle size distribution, and general composition and properties of the dust. Concentration and particle size distribution can be determined by a variety of methods based on one or more of the following principles : absorption, impingement and filtration, condensation of water vapour around the dust particles, or electrostatic thermal flocculation.

The collected dust may be estimated gravimetrically and by counting the particles.

**Absorption of the dust in a liquid**—Palmer's dust collector shown in Figure 43 consists of a U-tube partly filled with water. A definite volume of air is drawn through and the dust is trapped in the water and either filtered, dried and weighed, or if the dust is wholly or partly soluble in water the contents of the tube are evaporated and weighed. With dusts which do not dissolve in water a drop of the liquid can be examined under the microscope and the number and size of the particles can be determined.

\* Dr W. Matla kindly provided material and advice on this matter.



## ESTIMATION OF DUST

This method is cumbersome, the finer dust particles are not collected quantitatively and the properties of the dust may be modified by the water.

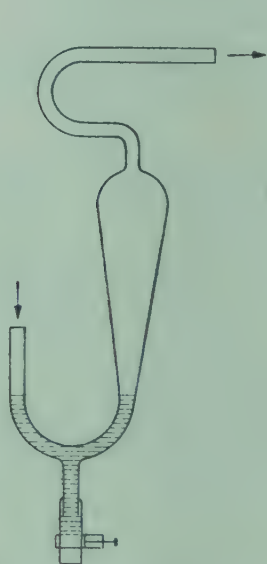


Figure 43. Palmer's apparatus for absorption of dust in liquid (JACOBS).

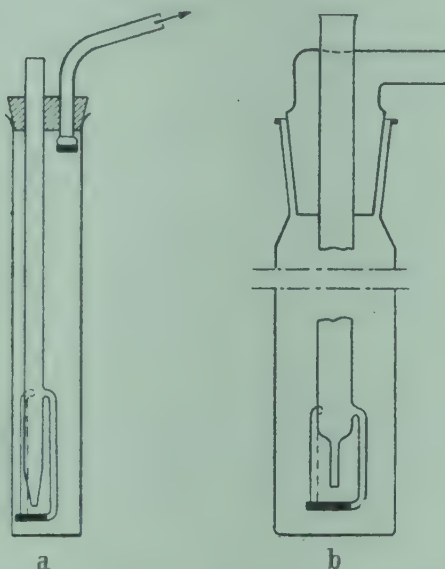


Figure 44 a, b. Apparatus for collection of dust in impingers (JACOBS).

**The impinger principle**—The air is projected at a relatively high velocity against a surface and absorbed in a liquid or fixed on the surface itself. Figure 44 illustrates the principle. The effect of the impinger depends on the character and the particle size of the dust. It is doubtful if fine dust is retained quantitatively.

In the konimeter a definite volume of air is drawn through a fine nozzle and deflected by a glass plate placed at a very short distance from the nozzle. The dust particles in the air are deposited on the glass surface by impingement, especially if the glass is covered with a thin layer of vaseline.

The dust spot is examined with a microscope. From the area of the dust deposit the number of dust particles per unit area and the volume of the sample, the number of dust particles per cc of air can be calculated. When the apparatus is used for one particular kind of dust the dust concentration can be derived from the light absorption of the dust spot with the aid of a calibration curve.

**Filtration methods**—The air is forced through a paper thimble (Figure 45) which is dried and weighed before and after the sampling. The method can be useful in determining high dust concentrations. The dust may also be caught in a filter consisting of fine crystals

*e.g.* of sugar, anthracene, or salicylic acid (Figure 46). After the sample is collected the crystals are dissolved and the dust is collected by filtration (sugar, salicylic acid), or sublimed, leaving the dust behind (anthracene).

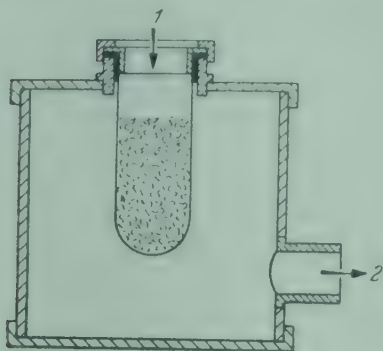


Figure 45. Apparatus for collection of dust in a paper thimble filled with wadding: 1 air inlet, 2 connection to suction pump (from JACOBS).

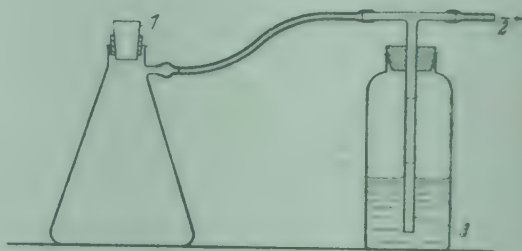


Figure 46. Sugar filter for dust analysis: 1 sugar filter in crucible, 2 connection to suction pump, 3 trap (from JACOBS).

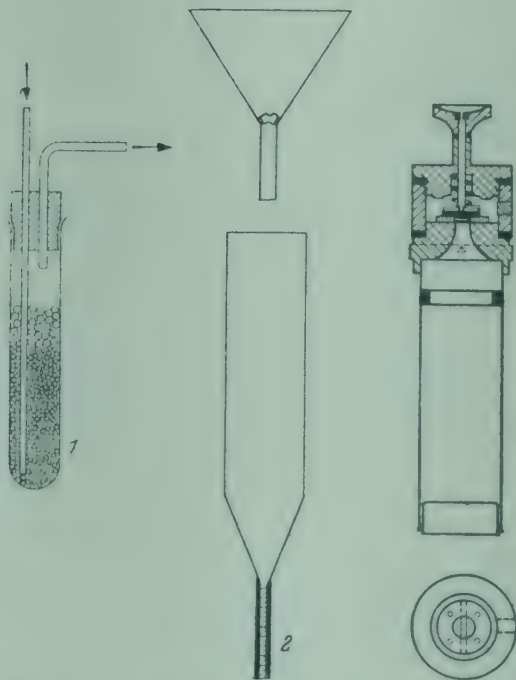


Figure 47. Oil filter for dust collection: 1 tube for absorption of dust, 2 centrifuge tube to collect and measure the captured dust, according to JACOBS.

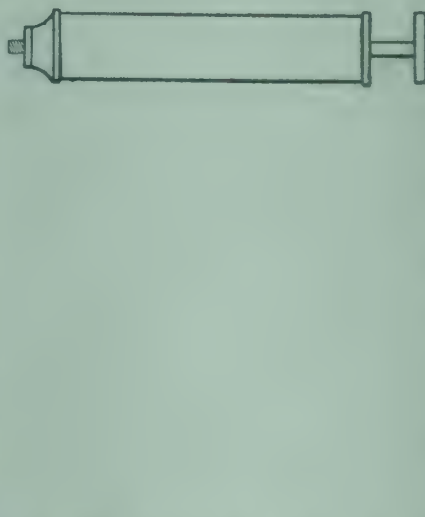


Figure 48. Owens' jet dust counter (JACOBS).

The principal disadvantage of these methods is that a gravimetric determination of the dust may easily lead to wrong conclusions, because of the importance of particle size distribution.

An oil filter may be used (Figure 47) in which the sample is drawn through a tube filled with glass beads wetted by oil, which catches the dust particles. The oil is dissolved in ether and the dust is collected by centrifuging.

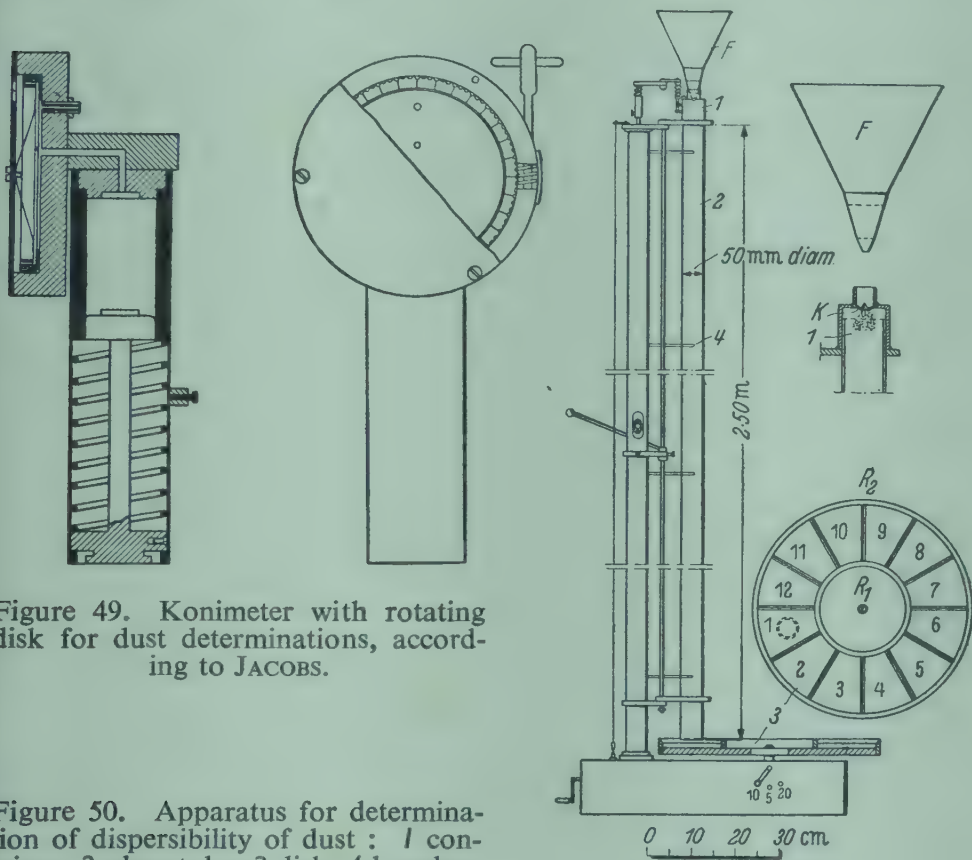


Figure 49. Konimeter with rotating disk for dust determinations, according to JACOBS.

Figure 50. Apparatus for determination of dispersibility of dust : 1 container, 2 glass tube, 3 disk, 4 knocker.

**Electrostatic dust collector**—The sample is drawn through a tube provided with electrodes and the electrically charged particles of dust precipitated by electrostatic forces, provided that the potential difference between the electrodes is sufficiently high.

**Condensation methods**—By reducing the pressure the sample is cooled below dew point, and the water vapour condenses, the dust particles acting as nuclei.

The OWENS' dust counter (Figure 48) combines this effect with the impinger principle. A definite volume of the sample is forced through a narrow slit past a cover glass by suddenly reducing its pressure.



The microscopic water drops, each containing a dust particle, are projected against the glass plate. The water evaporates and the dust remains on the glass surface. The sample is moistened by passing through moist filter paper.

It will be obvious that the water coated dust particles will be trapped more easily on the glass surface because they are heavier than the dust particles and because the moist particles adhere more easily to the glass.

The particles are deposited separately so that they may be counted more accurately than in the konimeter, where the particles have a tendency to agglomerate.

Modern dust counters are provided with a rotating disk, on which 12 cover glasses are mounted, so that it is relatively easy to make a series of determinations (Figure 49).

**Thermal precipitation**—The space around a heated wire is free from dust because the dust particles are repelled by the hot wire. When dust-laden air is passed along the wire the dust particles are deflected and deposited on a cover glass placed at a short distance from the wire. The deposit is examined under the microscope.

**Tyndallometer**—Light is dispersed and deflected by dust particles. The intensity of the dispersed light is a measure of the dust concentration. The instrument can be calibrated for a definite kind of dust, the intensity of the Tyndall light not only depending on the dust concentration, but also on the character and particle size distribution of the dust.

#### DETERMINATION OF PARTICLE SIZE DISTRIBUTION OF DUST

The particle size distribution of a powder or a sample of dust can be determined by several methods. The most important are sedimentation in a liquid and elutriation in a current of air or in a flowing liquid. For a description of the procedures reference should be made to the literature.

#### DISPERSIBILITY OF DUST

**Principle**—To characterize a powder the particle size distribution may be determined by sedimentation analysis or by elutriation. When the powder is dispersed in air it generally behaves as a much coarser material because of the coagulation of the particles.

In order to measure this property the powder is dropped through a long tube on to a rotating disk provided with raised flanges, the outer one of which can be removed. This disk is divided into twelve equal sectors over which the falling dust is distributed.

The amount of dust deposited on each sector is weighed. The fractions of dust reaching the disk are a function of time. The magnitude of each fraction is plotted against the corresponding time, giving a graph characterizing the dispersibility of the dust.

## DETERMINATION OF FREE QUARTZ

**Apparatus**—The apparatus is illustrated in Figure 50.

**Procedure**—Transfer 1 gm of the sample to the container 1 and operate the switch allowing the dust to fall and weigh the fractions collected in the sectors of the disk and plot the weighings against the time during which each fraction falls through the tube.

## DETERMINATION OF FREE QUARTZ IN ROCK AND STONE DUST

**Principle**—The silicates are decomposed with potassium pyrosulphate, feldspar and quartz are not dissolved. By treating the residue with phosphoric acid, feldspar is dissolved and quartz remains behind.

**Apparatus**—50 ml platinum dish porcelain filter crucible (A 1) and 400 ml beakers.

### REAGENTS

*Solid potassium pyrosulphate*

*Solid sodium hydroxide pellets*

*Hydrochloric acid*—1 volume concentrated acid diluted with 1 volume water

*Hydrofluoric acid*

*Phosphoric acid* sp gr 1.7

**Sample**—The sample should be finely pulverized to less than 50  $\mu$  and dried.

**Procedure**—Weigh approximately 500 mg of the sample to within 1 mg in the platinum crucible. Add 10 gm of potassium pyrosulphate and heat until a homogeneous melt has been obtained, taking care that the temperature does not rise beyond 700° C.

Cover the dish with a watch glass and allow it to cool.

Dissolve the cooled melt in a beaker containing 150-200 ml of water, add 10 gm sodium hydroxide and heat the mixture on the water bath for thirty minutes, then filter through a fine filter, wash with hot water, hot hydrochloric acid and finally once more with hot water. Place the filter paper and residue in a weighed platinum capsule and incinerate the filter paper. Ignite the ash at 500° C and weigh the crucible and residue of feldspar and free quartz.

Add 25 ml of phosphoric acid sp gr 1.17, heat the mixture to 250° C for thirty minutes. Allow the crucible to cool and cover with 300 ml of water in a beaker.

Heat until the liquid starts boiling, filter it through a weighed filter crucible and wash the precipitate with hot water. Dry the crucible and precipitate, ignite at 900° C and weigh. The ignition residue comprises free quartz.

Check the purity of the quartz by treating it with hydrofluoric acid in a platinum capsule heating to redness and weighing. The residue left must not exceed 0.6 per cent.

**Results**—The results are calculated in per cent by weight  $p$  free quartz in the dried original sample, using the formula :

$$p = \frac{a}{b} - 100$$

where  $a$  is the weight of the sample, and  $b$  is the weight of the quartz. The result should be expressed within 1 per cent.

**Note**—The reagents should be free from silicic acid. The hydrofluoric acid should leave no residue on evaporation.

If the sample contains carbon, it should just be ignited at a temperature of  $c$  500° C.

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Table 28. Heat Conductivity

Heat conductivity at room temperature (calories per sec. through a plate one centimetre thick, an area of one square centimetre and a temperature difference of  $1^{\circ}\text{C}$ )  $\times 10^3$ .

Metals		Various solids	
Aluminium ... ..	500	Asbestos ... ..	0.2—0.6
Brass (70Cu + 30Zn)	260	Basalt ... ..	5
Constantan (60 Cu + 40 Ni) ... ..	54	Brick, common red ...	1.5
Copper ... ..	1,000	Carbon ... ..	10
Iron, pure ... ..	160	Chalk ... ..	2
steel ... ..	110	Concrete, cinder ...	0.8
Lead ... ..	80	stone ... ..	2
Mercury ... ..	20	Cork ... ..	0.1—0.7
Nickel ... ..	140	Cotton wool ... ..	0.04
Platinum ... ..	170	Diatomaceous earth ...	0.1
Platinum-rhodium ...	70	Ebonite ... ..	0.1—0.4
(90-10) ... ..		Flannel ... ..	0.2
Silver ... ..	1,000	Glass ... ..	1—2
Tin ... ..	155	Graphite ... ..	12
Wood's alloy ... ..	30	Gypsum ... ..	3
Zinc ... ..	265	Ice ... ..	5
Liquids		Lamp black ... ..	0.07
Benzene ... ..	0.3	Magnesia (MgO) ...	0.16—0.45
Ether ... ..	0.3	Paper ... ..	0.1—0.5
Ethanol ... ..	0.4	Porcelain ... ..	2.5
Glycerol ... ..	0.6	Portland cement ...	0.7
Water ... ..	1.4	Rubber ... ..	0.5
Gases		Sand, dry ... ..	1
Air ... ..	0.06	Sawdust ... ..	0.1
Ammonia ... ..	0.05	Silk ... ..	0.1
Carbon dioxide ... ..	0.03	Slate ... ..	5
Carbon monoxide ...	0.05	Wax, bees ... ..	0.1
Ethylene ... ..	0.04	Wood ... ..	0.1—0.3
Hydrogen ... ..	0.03		
Nitrogen ... ..	0.05		
Oxygen ... ..	0.06		

Compound	Sp. gr. (water=1) of liquid	Sp. gr. (air=1) of vapour	Boiling point, °C	Specific heat of liquid at 20° C	Vapour pressure at 20° C mm Hg	Heat of vaporiza- tion at boiling point kcal/kg	Heat of combustion (high)	Flash point, °C	Ignition tempera- ture, °C	Explosive limits in air Vol per. cent	
										lower	upper
Acetaldehyde	0.78	1.52	21	—	760	136	6,300	-27	185	4	57
Acetone	0.79	2.00	56.5	0.53	185	124.5	7,430	-18	538	2.6	13
Acetylene	—	0.91	-84	—	—	—	12,000	gas	335	2.5	80
Ammonia	—	0.60	-33.4	—	—	327	5,075	gas	650	15	26
Aniline	1.02	3.22	184	0.50	<0.5	104	8,720	75	538	—	—
Anthracene	1.25	1.15	340	—	—	—	9,540	121	472 in O <sub>2</sub>	0.63	—
Benzene	0.88	2.77	80	0.41	75	94.3	10,000	-11	538	1.4	8.0
Carbon disulphide	1.3	2.64	46	0.24	298	84	3,400	-30	100	1.0	50
Carbon monoxide	—	0.97	-190	—	—	50.5	2,440	gas	650	12.5	74
Cyclohexane	0.78	2.90	80	—	77	86	11,140	-17	296	1.3	8.4
Ethane	—	1.05	-88	—	—	258	12,400	gas	510	3.0	12.5
Ethanol	0.79	1.59	78	0.58	44	204	7,140	13	371	3.5	19
Ether (diethyl)	0.71	2.56	35	0.54	442	84	8,795	-45	180	1.9	37
Ethyl acetate	0.90	3.04	77	0.46	73	88	5,540	-4	427	2.2	11.5
Ethylene	—	0.98	-103	—	—	—	12,300	gas	450	2.8	29
Ethylene oxide	0.89	1.52	11	—	—	139	6,860	<-7	430	3.0	80
Gas (coal gas)	—	—	—	—	—	—	250-370	gas	650	5.3	31
Gas oil	<1	—	—	—	—	—	10,800	65	338	6.0	13.5
Hydrocyanic acid	0.70	0.9	26	—	—	210 (20°C)	6,080	-32	538	6	40
Hydrogen	—	0.07	-253	—	—	108	33,900	gas	585	4	74
Hydrogen sulphide	—	1.19	-60	—	—	132	3,820	gas	260	4.3	46
Methane	—	0.55	-162	—	—	138	13,300	gas	537	5	15
Methanol	0.79	1.11	64.7	0.60	96	263	5,400	11	427	6	36.5
Naphthalene	1.15	4.42	218	—	—	76	9,600	80	559	0.9	5.9
Nitrobenzene	1.2	4.25	211	0.33	—	79	6,025	88	482	—	—
Petroleum (light)	—	4	125	0.60	—	—	10,500	-43	257	1.3	7.5
Petroleum (heavy)	—	4.8	140-200	0.53	—	—	11,500	—	—	—	—
Pyridine	0.98	2.73	115	0.43	—	107	8,340	20	482	1.8	12.5
Toluene	0.87	3.14	111	0.39	23	87	10,200	4	552	1.3	7.0
O-Xylene	0.88	3.66	144	0.40	10	83	10,300	17	482	1.0	5.3

Table 30. Classification of flammable liquids by the National Fire Protection Association according to their flash points (closed cup test)

Class I Flash point below -4° C		Class II Flash point between -4° C and 21° C		Class III Flash point between 21 and 93½° C
Insoluble in water	Soluble in water	Insoluble in water	Soluble in water	Insoluble in water
Ether	Acetone	Lacquers	Acetaldehyde	Standard solvents
Carbon disulphide		Amyl acetate	Methanol	Kerosene
Petroleum		Toluene	Ethanol	Pentanol
Benzene		Ethyl acetate	Pyridine	Creosote oil
Collodium				Turpentine
				Fuel oil
				Aniline
				Tetralin
				Naphthalene

Table 31. General classes of fires and their extinguishment

Class	Burning material	Initial extinguisher	
		type	characteristics
A	Ordinary combustible materials, such as wool, paper, textiles, rubbish	Sand	Shutting off the air
		Water	Cooling or quenching with water (high specific heat and heat of evaporation)
		Soda-acid extinguisher	
B	a Flammable liquids not soluble in water such as petroleum, oils, benzole, paint, tar, grease in open vessels or on floors	Carbon dioxide	Carbon dioxide is suitable inside buildings on valuable articles and apparatus
		Foam	Blanketing or smothering effect by shutting off the air by a blanket of foam containing bubbles of carbon dioxide
		Asbestos blanket	
	b Flammable liquids soluble in water, such as alcohol and ether	Water	Quenching by diluting with water. Shutting off the air by covering the container; or with a stable foam

(Continued on next page)



Table 31—continued

Class	Burning material	Initial extinguisher	
		type	characteristics
C	In or near electrical equipment	Carbon tetra-chloride Methyl bromide	These non-conducting liquids will not damage machinery or electrocute the man ; they are only to be used in ventilated areas because of the toxicity of their vapour
		Sometimes carbon dioxide	Never use water or foam : danger of electrocution
D	Combustion in motors	Carbon tetra-chloride, Methyl bromide, sometimes Carbon dioxide	Sand, water and foam damage the apparatus
E	a Combustible gas escaping freely	Any liquid or gaseous extinguishing agent	Shut off the gas supply. 'Cut off' the flame by a powerful directed stream of water, carbon dioxide or carbon tetrachloride. Foam has no effect. Sometimes it is advisable to let the gas burn out instead of extinguishing the flame and thereby risking poisoning, asphyxiation or the formation of an explosive mixture of gas and air by the escaping gas
	b Combustible gas formed by the reaction of water with sodium, potassium, carbides, phosphides etc	Dry sand	Water or foam promote the fire. Halogenated hydrocarbons may give violent reactions with light metals

When a fire is past the initial stage the fire brigade may be forced to apply water even in cases when this is contradictory to the recommendations in this table. When a fire starts in or near electrical apparatus the current must be cut off.

Carbon dioxide has little or no effect in the open ; inhalation may cause unconsciousness and death ; the stream of carbon dioxide may spread the burning material ; the fire may start anew after it has been extinguished by carbon dioxide ; light metals burn in carbon dioxide.

*Nat. Safety News* 59 (1949) 22

*Quart. Safety Summary* 20 (1949) 3

*Rijksinspectie voor het Brandweerwezen's-Gravenhage*

Table 32. Storage of High Purity (Analar) Chemicals

<i>Chemical substance</i>	<i>Maximum quantities to be stored in a bottle (gm)</i>
<i>Pure iron, zinc, aluminium, magnesium (powder)</i>	100
<i>CaO, ZnO, MgO, Bi<sub>2</sub>O<sub>3</sub> ... ..</i>	100
<i>Sodium peroxide ... ..</i>	50
<i>Soda lime ... ..</i>	250
<i>Barium hydroxide ... ..</i>	100
<i>Hydrogen peroxide (30 per cent) ... ..</i>	200
<i>Ferric chloride ... ..</i>	100
<i>Magnesium chloride ... ..</i>	250
<i>Antimony chloride ... ..</i>	50
<i>Zinc chloride ... ..</i>	100
<i>Silicon tetrachloride ... ..</i>	25
<i>Sulphur monochloride ... ..</i>	50
<i>Titanium tetrachloride ... ..</i>	25
<i>Phosphorus chlorides ... ..</i>	250
<i>Zinc, magnesium or ferrous ammonium sulphates</i>	100
<i>Ammonium persulphate ... ..</i>	50
<i>Sodium sulphide ... ..</i>	100
<i>Ammonium sulphide ... ..</i>	500
<i>Sodium bisulphite ... ..</i>	500
<i>Ammonium sulphite ... ..</i>	250
<i>Copper, calcium nitrates ... ..</i>	100
<i>Ammonium and sodium carbonate and bicarbonate ... ..</i>	250
<i>Potassium thiocyanate ... ..</i>	100
<i>Zinc iodide ... ..</i>	25
<i>Potassium iodide, iodate and biiodate ... ..</i>	100
<i>Potassium cyanide ... ..</i>	50
<i>Ammonium acetate ... ..</i>	100

Table 33. Irritants and Toxic Smokes

Substance	Minimum concentration causing irritation, mg/m <sup>3</sup>	Concentration which cannot be tolerated longer than 1 min mg/m <sup>3</sup>	Fatal in 1 min mg/m <sup>3</sup>	Amount volatilized at room temperature mg/m <sup>3</sup>
<i>Acrolein</i> ... ..	7*	50—60	2,000	20,000
<i>Allyl isothiocyanate</i> ... ..	—	40	—	—
<i>Ammonia</i> ... ..	300	> 300	3,500—7,000	gas
<i>Arsenic trichloride</i> ... ..	—	200	25,000	85,000
<i>Benzoylchloride</i> ... ..	—	108	—	—
<i>Benzyl bromide</i> ... ..	4*	60	6,000	3,400
<i>Benzyl iodide</i> ... ..	2*	30	3,000	1,200
<i>Bromacetone</i> ... ..	1*	10—50	4,000	75,000
<i>Bromethylmethyl ketone</i> ... ..	1,6—11*	16	6,000	34,000
<i>Cacodyl chloride</i> ... ..	—	30	—	—
<i>Cacodyl cyanide</i> ... ..	—	15	—	—
<i>Cacodyl oxide</i> ... ..	—	45	—	—
<i>Chlorine</i> ... ..	10	100	7,500	gas
<i>Chlorinated methyl formate</i> ... ..	—	90	—	—
<i>Chloracetone</i> ... ..	18*	100—110	3,000	120,000
<i>Chloracetophenone</i> ... ..	0.3*	4.5	4,000	105
<i>Chloropicrin</i> ... ..	2—19*	50—100	2,000	180,000—290,000
<i>Cyanogen bromide</i> ... ..	5	60	2,000	200,000
<i>Cyanogen chloride</i> ... ..	—	50	—	b.pt 16° C
<i>Diphenylamine chlorarsine</i> ... ..	0.01	0.4	—	0.02
<i>Diphenylchlorarsine</i> ... ..	0.01	1	4,000	0.3
<i>Diphenylcyanarsine</i> ... ..	0.01	0.25	4,000	0.1
<i>Ethyl arsenious oxide</i> ... ..	—	5—7	—	—
<i>Ethyl bromacetate</i> ... ..	3—5*	40—55	3,000	21,000
<i>Ethyl chlorosulphonate</i> ... ..	2	50	3,000	—
<i>Ethyl chlorarsine</i> ... ..	1	8—17	3,000	22,000
<i>Ethyl iodoacetate</i> ... ..	1.4*	15	1,500	3,100
<i>Iodoacetone</i> ... ..	12*	> 200	—	3
<i>Methyl arsenious oxide</i> ... ..	—	5	—	—
<i>Methyl chlorosulphonate</i> ... ..	2	40—60	2,000	—
<i>Methyl dichlorarsine</i> ... ..	2	25	3,000	75,000
<i>α-Naphthylldichlorarsine</i> ... ..	—	5	—	—
<i>p-Nitrophenyldichlorarsine</i> ... ..	—	2.5	—	—
<i>Phenylcarbylaminchloride</i> ... ..	3	25	3,000	2,100
<i>Phenyldichlorarsine</i> ... ..	—	16	—	—
<i>Xylyl bromide</i> ... ..	1.8*	20—56	6,000	600
<i>Phosgene</i> ... ..	3	20	450	gas

\*Lachrymatory properties



Table 34. Minimum concentration (ppm) causing the effect mentioned

Substance	Detectable odour*	Irritation of the throat	Coughing	Slight symptoms after several hours exposure	No. serious effects after 1 hr exposure	Danger after 30 min exposure	Death within a few min	Maximum allowable concentration	Description of odour
Acetaldehyde	2-3	—	—	—	—	—	—	200	Pungent
Ammonia	50	400	1,700	—	300-500	—	5,000-10,000	100	Sharp pungent
Amyl acetate	0.1	—	—	2,000	—	—	—	200	Odour of banana
Aniline	—	—	—	7-53	100-160	—	—	5	—
Arsine	—	—	—	3	6	15	1,500	0.05	Unpleasant garlic odour probably caused by impurities
Benzene	—	—	—	1,500-3,000	3,000-4,700	6,000-9,000	19,000-20,000	35	Pleasant at low and disagreeable at higher concentrations
Carbon dioxide	—	—	—	11,000-17,000	30,000-40,000	50,000-67,000	200,000	5,000	Acid taste
Carbon disulphide	1	—	—	300-400	500-1,600	1,000-4,000	—	20	Very disagreeable odour caused by impurities
Carbon monoxide	70	—	—	50-100	600	3,000-5,000	13,000-50,000	100	Slightly sweetish odour recalls that of chloroform
Carbon tetrachloride	3.5	15	30	1	4	50-100	1,000-2,000	1	Pungent and irritating odour
Chlorine	—	No warning properties	—	—	—	—	100	1	Extremely irritating to all parts of respiratory tract
Dimethyl sulphate	35	35	—	20	50-100	100-150	1,000-2,000	5	Sharp smell, acid taste
Hydrogen chloride	1	—	—	—	50	500-700	270	10	Odour of bitter almonds
Hydrogen cyanide	0.5	50-100	100	—	200-300	—	1,000-2,000	20	Smell of bad egg
Hydrogen sulphide	8	60	100	40-80	200-300	100-150	—	1	Odour of bitter almonds
Nitrobenzene	—	—	—	25	—	—	200-300	25	Typical, not irritating in concentrations which are hazardous
Oxides of nitrogen	—	—	—	—	—	—	—	—	Slightly pungent, irritating
Ozone	0.5	—	—	—	—	—	—	1	Faint odour of ensilage or freshly cut hay
Phosgene	1.5	3	5	—	25	50	450	1	—
Sulphur dioxide	3.5	8-12	20	—	50-100	200-500	—	10	Characteristic pungent odour

\* The sense of smell is rapidly affected. Two or more odorous substances may cancel each other out. This compensation will mean that two odorous substances smelt together may be odourless.

McCORD, C. P. and WITHERIDGE, W. N. *Odors, physiology and control* New York, 1900  
 HENDERSON, Y. and HAGGARD, N. W. *Noxious gases* New York, 1943  
 CLINTON, M. A. P. I. Toxicological reviews. *American Petr. Inst.* 1948, 1949  
 FLURY, F. and ZERNIK, F. *Schädliche Gase* Berlin, 1931

Table 35. Comparative toxicity of halogenated hydrocarbons based on permissible concentrations in ppm (Carbon tetrachloride = 1)

<i>Ethyl chloride</i> ... ..	0.05
<i>Dichloromethane</i> ... ..	0.1
<i>Ethyl bromide</i> ... ..	0.25
<i>Dichlorethylene</i> ... ..	0.25
<i>Chloroform, 1, 1-dichlorethane, methyl chloride, tetrachlorethylene, trichlorethylene</i> ... ..	0.5
<i>1, 2-dichloropropane, 1, 2-dichlorethane, monochlorobenzene</i> ...	0.67
<i>Carbon tetrachloride</i> ... ..	1.0
<i>o-dichlorobenzene</i> ... ..	1.0
<i>Methyl bromide</i> ... ..	2.5
<i>1, 1, 2, 2-Tetrachlorethane</i> ... ..	10.0
<i>Chlorine, bromine</i> ... ..	50.0

Table 36. Zones of Toxicity

<i>Parts per million</i>	<i>Contaminants</i>
< 0.1	Arsine, hydrogen selenide, phosphine, radioactive gases
0.1—2	Acrolein, bromine, chlorine, dimethyl sulphate, iodine, nickel carbonyl, nitrobenzene, nitroglycerin, ozone, phosgene, phosphine, phosphorus trichloride, tetryl, trinitrotoluene, dinitrotoluene
2—20	Hydrogen fluoride, aniline, dimethylaniline, formaldehyde, hydrochloric acid, nitric acid, sulphuric acid, sulphur dioxide, tetrachlorethane, carbon disulphide, hydrogen cyanide, hydrogen sulphide
20—100	Oxides of nitrogen, methyl bromide, cellosolve acetate, methyl cellosolve, monochlorobenzene, dichlorobenzene, ammonia, benzene, carbon monoxide, carbon tetrachloride, chloroform
100—500	Pentanol, butanol, methanol, dichloromethane, tetrachlorethylene, toluene, trichlorethylene, turpentine, xylene, ethylene oxide, acetates, ether, styrene monomer, cellosolve
500—2,500	Butadiene, ethyl alcohol, petroleum, methyl cyclohexane, vinylchloride
> 2,500	Carbon dioxide, acetylene

Table 37. Maximum permissible concentrations of poisonous and irritant substances adopted at the Meeting of the American Conference of Governmental Industrial Hygienists, Chicago, April 1950

Contaminant	Permissible concentration	
Mineral dusts (0.5—10.0 $\mu$ )... ..	10 <sup>6</sup> particles per ft <sup>3</sup> (standard light field count)	
Asbestos ... ..	5	
Cement, alundum, carborundum... ..	50	
Silica (less than 5 per cent free SiO <sub>2</sub> ) ... ..	50	
Silica (5—50 per cent free SiO <sub>2</sub> ) ... ..	20	
Silica (more than 50 per cent free SiO <sub>2</sub> ) ... ..	5	
Slate and Mica (less than 5 per cent free SiO <sub>2</sub> ) ... ..	50	
Talc ... ..	20	
Total dust (less than 5 per cent free SiO <sub>2</sub> ) ... ..	50	
Metallic dusts and fumes ... ..	mg/m <sup>3</sup>	
Antimony, arsenic, barium ... ..	0.5	
Cadmium ... ..	0.1	
Chromium (acid, chromate or dichromate as CrO <sub>3</sub> ) ... ..	0.1	
Lead ... ..	0.15	
Manganese ... ..	6	
Mercury, selenium, tellurium ... ..	0.1	
Iron, magnesium and zinc oxide fumes ... ..	15	
Miscellaneous dusts and fumes ... ..	mg/m <sup>3</sup>	
Chlorodiphenyl ... ..	1	
Cyanide as CN ... ..	5	
o-Dinitrocresol ... ..	0.2	
Fluorides ... ..	2.5	
Pentachloro naphthalene or phenol ... ..	0.5	
Phosphorus (yellow) ... ..	0.1	
Phosphorus penta chloride or sulphide ... ..	1	
Tetryl, trinitrotoluene, dinitrotoluene ... ..	1.5	
Trichloronaphthalene ... ..	5	
Gases and vapours	ppm	mg per m <sup>3</sup> (conversion to nearest whole number value from ppm)
Acetate, amyl ... ..	200	1,100
n-butyl ... ..	200	1,000
ethyl ... ..	400	1,500
methyl ... ..	200	600
propyl ... ..	200	800
Acetones (see Ketones) ... ..	5,000	5,300
Acetylene (based on lower explosive limit)		
Hydrochloric acid ... ..	5	8
Hydrogen cyanide ... ..	10	10
Hydrogen fluoride ... ..	3	3
Hydrogen sulphide ... ..	20	30
Sulphuric acid ... ..	0.25	1

(Continued on next page)



Table 37—continued

Gases and vapours	ppm	mg per m <sup>3</sup> (conversion to nearest whole number value from ppm)
Acrolein (see Aldehydes) ... ..		
Acrylonitrile (vinyl cyanide) ... ..	20	45
Alcohol, isoamyl ... ..	100	350
<i>n</i> -butyl ... ..	100	300
ethyl ... ..	1,000	1,900
methyl ... ..	200	250
isopropyl ... ..	400	1,000
Acetaldehyde ... ..	200	400
Acrolein ... ..	0.5	1
Formaldehyde ... ..	5	6
Ammonia ... ..	100	70
Aniline ... ..	5	20
Arsine ... ..	0.05	0.2
Benzene ... ..	35	115
Bromine ... ..	1	6
1, 3-butadiene ... ..	1,000	2,250
Carbon dioxide ... ..	5,000	9,000
Carbon disulphide ... ..	20	60
Carbon monoxide ... ..	100	100
Carbon tetrachloride ... ..	50	300
Cellosolve ... ..	200	750
Chlorine ... ..	1	3
2-chlorobutadiene ... ..	25	9
Chloroform ... ..	100	500
1-chloro-1-1-nitropropane ... ..	20	100
Cyclohexane (hexene, propane and propene)	400	—
Cyclohexanol ... ..	100	400
<i>o</i> -dichlorobenzene ... ..	50	300
Dichloro (mono or di) fluormethane ...	1,000	—
Dichlorotetrafluorethane ... ..	1,000	—
1, 1-dichlorethane ... ..	100	400
1, 2-dichlorethylene ... ..	200	800
Dichlorethyl ether ... ..	15	19
Dichloromethane ... ..	500	1,750
1, 1-dichloro-1-nitroethane ... ..	10	60
1, 2-dichloropropane ... ..	75	350
Dimethylaniline ... ..	5	25
Dimethyl sulphate ... ..	1	5
Dioxane ... ..	100	350
Ether, ethyl... ..	400	1,200
Ethyl benzene, ethyl bromide ... ..	200	—
Ethyl chloride ... ..	1,000	2,700
Ethylene chlorhydrin ... ..	5	15
Ethylene dichloride (1, 2-dichlorethane) ...	75	300
Ethylene oxide ... ..	100	200
Ethyl formate, ethyl silicate ... ..	100	—
Heptane, hexane ... ..	500	—
Iodine ... ..	1	10

(Continued on next page)

Table 37—continued

Gases and vapours					ppm	mg per m <sup>3</sup> (conversion to nearest whole number value from ppm)
<i>Ketone, dimethyl (acetone)</i> ... ..					500	1,200
<i>methyl butyl (hexanone)</i> ... ..					100	400
<i>methyl ethyl (butanone)</i> ... ..					250	750
<i>methyl isobutyl (hexone)</i> ... ..					100	400
<i>methyl isobutenyl (mesityloxiide)</i> ... ..					50	200
<i>methyl propyl (pentanone)</i> ... ..					200	700
<i>(Methyl) cyclohexanone</i> ... ..					100	—
<i>Isophorone (trimethyl cyclohexanone)</i> ... ..					25	150
<i>Methyl bromide</i> ... ..					20	80
<i>Methyl cellosolve (acetate)</i> ... ..					25	—
<i>Methyl chloride, methyl formate</i> ... ..					100	—
<i>Methyl cyclohexane</i> ... ..					500	2,000
<i>Monochlorobenzene</i> ... ..					75	350
<i>Nickel carbonyl</i> ... ..					1	7
<i>Nitroethane, nitromethane</i> ... ..					100	—
<i>Nitroglycerin</i> ... ..					0.5	5
<i>2-Nitropropane</i> ... ..					50	200
<i>Nitrobenzene</i> ... ..					1	5
<i>Nitrogen oxides (other than N<sub>2</sub>O)</i> ... ..					25	—
<i>Ozone</i> ... ..					1	2
<i>Petroleum</i> ... ..					500	—
<i>Phosgene</i> ... ..					1	4
<i>Phosphine</i> ... ..					0.05	0.1
<i>Phosphorus trichloride</i> ... ..					0.5	2.5
<i>Isopropylether</i> ... ..					500	200
<i>Stibine</i> ... ..					0.1	0.5
<i>Styrene monomer</i> ... ..					200	900
<i>Sulphur dioxide</i> ... ..					10	25
<i>1,1,2,2-Tetrachlorethane</i> ... ..					5	35
<i>Tetrachlorethylene (perchlorethylene)</i> ... ..					100	700
<i>Toluene</i> ... ..					200	750
<i>Toluidine</i> ... ..					5	20
<i>Trichlorethylene</i> ... ..					100	550
<i>Turpentine</i> ... ..					100	500
<i>Vinyl chloride</i> ... ..					500	1,200
<i>Xylene</i> ... ..					200	900
Radiation threshold					Curie/l	Roentgen/week
<i>Radon</i> ... ..					10 <sup>-11</sup>	—
<i>Thoron</i> ... ..					10 <sup>-11</sup>	—
<i>X-ray</i> ... ..					—	0.3
<i>Radium (gamma radiation)</i> ... ..					—	0.3

mg/m<sup>3</sup> = mol.wt./24.45 ppm

*Note*—Although this table gives valuable information about the toxicity of the more important compounds which can be present as contaminants of the atmosphere, these data are not absolute in the sense of physical data which can be defined and determined with accuracy. These safety limits are based on general experience. In the course of time they have been revised, and they will be revised later, because new experiences will undoubtedly lead to corrections and improvements.

SCHRENK, H. H. Interpretation of permissible limits in the breathing of toxic substances in air *Bur. Mines Inf. Cir.* 7457, 1948

Table 38. Ventilation rates required to dilute 1 gram of a solvent per minute to the maximum allowable concentration

Compound	Molecular weight	Specific gravity	Maximum permissible concentration mg/m <sup>3</sup>	m <sup>3</sup> air per min per gm solvent per min
<i>Ammonia (liquid)</i> ...	17	0.60	70	15
<i>Amyl acetate</i> ...	130	0.87	1,100	0.9
<i>Amyl alcohol</i> ...	88	0.82	350	3.0
<i>Aniline</i> ...	93	1.02	20	50
<i>Benzene</i> ...	78	0.88	115	9.0
<i>Carbon disulphide</i> ...	76	1.26	60	16
<i>Carbon tetrachloride</i> ...	154	1.58	300	3.3
<i>Dichlorobenzene</i> ...	147	1.32	300	3.3
<i>Ethyl alcohol</i> ...	46	0.81	1,900	0.5
<i>Mercury</i> ...	201	13.6	0.1	10,000
<i>Methyl bromide</i> ...	95	1.73 (0°C)	80	13
<i>Monochlorobenzene</i> ...	113	1.11	350	3
<i>Nitrobenzene</i> ...	123	1.20	5	200
<i>Toluene</i> ...	92	0.86	750	1.3
<i>Trichlorethylene</i> ...	131	1.48	550	1.8
<i>Xylene</i> ...	106	0.88	900	1.2



Table 39. The most important noxious gases, vapours, mists and fumes, their effects and treatment

Compound	Means of absorption	Toxic effects	First aid
Acetic acid	R	Irritation of the mucous membranes and conjunctivae	Keep patient warm and quiet
Acetone	R	Mild narcotic action. Irritation of the mucous membranes. Afterwards headache. High concentrations give a feeling of discomfort and a desire for fresh air	Transfer to fresh air and give rest
Acetylene	R	Toxic effects mainly due to impurities such as phosphine and admixtures <i>e.g.</i> carbon monoxide. Mental confusion, non-reacting pupils, slow breathing, vomiting, cyanosis, low irregular pulse	Remove patient to fresh air and keep him warm and quiet. Rest is necessary. Give oxygen and if necessary artificial respiration. <i>No stimulants</i>
Alcohol	R and D	Irritation of the mucous membranes; headache, dizziness, lassitude, lack of concentration, inebriation; in the long run, degeneration of the liver	Keep patient warm, give an emetic and then hot coffee
Ammonia	R	<i>Acute</i> : a feeling of asphyxiation, severe irritation of the eyes, lips, mouth, throat and lungs. Vomiting, coughing, difficult breathing and chest pain. Chronic poisoning is unknown. In rare instances permanent scarring, particularly of the eyes	Fresh air, warmth, complete rest. Remove wet clothing. Flush skin with water (do not rub) and dilute acetic acid. Flush eyes with water, followed by abundant irrigation with physiological saline or isotonic boric acid solution and then local application of anaesthetic. If respiration is affected, inhalations from 5-7 per cent carbon dioxide in oxygen should be given
Aniline	R and S	Blood poison, affects the nervous system, produces cyanosis, excitement, fatigue, loss of appetite, headache	If spilled on the clothes, a bath should be taken and the clothes changed. If inhaled : fresh air and absolute rest. Do not give alcohol or oils
Arsine	R	<i>Acute</i> : intense headache, nausea and vomiting, dizziness, jaundice, hematuria, swollen liver and spleen. Lesions of the eye (cornea) with rapid tissue necrosis. <i>Chronic</i> : paleness, abdominal pains, diarrhoea, difficult breathing, emaciation, trembling limbs, skin eruption, falling out of hairs and nails	Fresh air, complete rest : call a doctor at once
Benzene and its homologues	R and S	<i>Acute</i> : drunkenness, excitement, pallor followed by blushing, breathlessness, ringing in ears, dizziness, vomiting, headache, disturbed vision, staggering gait. In severe cases : cramp, coma and death <i>Chronic</i> : weakness, headache, dizziness, increasing nervousness, loss of weight, vomiting, stomach disturbance, bleeding from the gums, nose, rectum or uterus, and altered menses of the female. Marked but varied and irreversible changes in the blood picture (aplastic anaemia, leucopenia <i>etc.</i> ). Injury to blood vessels, heart, liver, kidneys. Susceptibility to infections	<i>Acute</i> : fresh air, complete rest, keep patient warm. Oxygen and artificial respiration if needed. Hot coffee or tea as a stimulant <i>Chronic</i> : nourishing food with an excess of animal fats and a high calcium content. Liver extract and iron, blood transfusions, vitamin C. Remove permanently from contact with benzene

R—respiratory tract

S—skin

D—digestive tract

(Continued on next page)

Table 39—continued

Compound	Means of absorption	Toxic effects	First aid
Bromine	R	Violent irritation of air passage and eyes, bronchitis and conjunctivitis, sensation of suffocation, skin eruptions, brownish stain on skin and mucous membranes	Fresh air, keep patient warm with blankets and hot-water bottles. Constricting clothing should be loosened. Oxygen should be administered in all cases. Absolute rest is always essential. Olive oil may be effective for the eyes. Do not apply artificial respiration
Calcium cyanide Cyanamide	R	Severe irritation of nose, throat and skin ; headache, shortness of breath, rapid pulse, vasodilation with lowered blood pressure by consumption of alcohol	As cyanides
Carbon dioxide	R	This is a simple asphyxiant. The symptoms preceding asphyxia are : headache, dizziness, rapid breathing, dyspnea, drowsiness, muscular weakness, flushing of face, ringing in ears	Fresh air. Keep patient warm with blankets and hot-water bottles. Artificial respiration (administer oxygen)
Carbon disulphide	R	<i>Acute</i> : headache, dizziness, nausea, reeling, talkativeness, laughing, crying, or stupor, coma, death <i>Chronic</i> : irritability, dizziness, trembling, drowsiness, chronic fatigue, insomnia, excitability followed by apathy, depression and mental confusion ; muscular pain, weakness of muscles (legs, arms) ; loss of appetite and weight, indigestion, constipation ; disturbances of vision ; loss of libido	<i>Acute case</i> : artificial respiration with oxygen. Coffee <i>Chronic</i> : Diet with a high vitamin content with the vitamin B complex as an adjunct. Psychiatric and ophthalmologic attention
Carbon monoxide	R	Headache, throbbing in temples, dizziness, rapid pulse and breathing, loss of muscular control, confusion followed by unconsciousness, red face	Fresh air, keep patient warm. Artificial respiration with oxygen therapy. Do not give stimulants
Carbon tetra-chloride	R	Irritation of nose, eyes and throat, headache, dizziness, pallor, vomiting, excitement, visual disturbances, weak pulse, narcosis ; jaundice, nephritis, dermatitis	Artificial respiration and oxygen if necessary. The diet should contain a high proportion of carbohydrates with a low fat and meat protein ratio
Chlorine	R	Irritation of mucous membranes, flood of tears, coughing, suffocation, cold sweats, weak pulse	As for bromine
Chloroform	R	<i>Acute</i> : irritation of mucous membranes, flood of tears and saliva, rapid pulse, vomiting, narcosis <i>Chronic</i> : indigestion, loss of weight, insomnia, nervous disturbances	Keep warm and quiet. Artificial respiration and oxygen if necessary
Cyanogen compounds (cyanides, hydrogen cyanide)	R, S and D	Dizziness, headache, vomiting, constriction of the throat, palpitation of the heart, rapid breathing, followed by asthmatic symptoms, shortness of breath, a feeling of distress, cramps ; finally unconsciousness	After inhalation of the poison give amyl nitrite inhalation. If swallowed gastric lavage with sodium thiosulphate 50 gm/l or potassium permanganate solution (1 gm/l). Oxygen inhalation or artificial respiration if necessary. Call doctor at once

R—respiratory tract

S—skin

D—digestive tract

(Continued on next page)

Table 39—continued

Compound	Means of absorption	Toxic effects	First aid
<b>Chromium compounds</b>	R and S	Lesions of the skin and the mucous membranes followed by necrosis of the tissues (perforation of the nasal septum)	If the lesions are small and superficial scrub thoroughly with sodium bisulphite solution, 50 gm/l, or sodium chloride solution. Then the wound is treated like any abrasion of similar severity. Deep ulcers : 3-5 days wet dressings of sodium bisulphite, then 3-5 days wet dressings of solution of potassium and sodium tartrate 50-100 gm/l. See a doctor
<b>Dimethyl sulphate</b>	S and R	Corrosion of the skin and mucous membranes, hoarseness, bronchitis, pulmonary oedema	
<b>Dichloroethane</b>	R	Etching of the mucous membranes, narcosis and poisoning of the nerves	For epigastric cramps calcium gluconate is administered
<b>Ether</b>	R	As alcohol	As alcohol
<b>Ethylene</b>	R	As carbon monoxide	As carbon monoxide
<b>Formaldehyde</b>	R	<i>Acute</i> : irritation of the eyes, nose and lungs, sometimes headache <i>Chronic</i> : Brownish discoloration of the finger tips, painful nailbeds	Inhalation of vapour of dilute ammonia
<b>Hydrochloric acid</b>	R	<i>Acute</i> : irritation of the mucous membrane and skin, coughing, burning, or stinging of the throat, conjunctival inflammation and slight corneal damage <i>Chronic</i> : loss of appetite and weight, headache, insomnia, nasal irritation, sore throat, and dry cough, dental caries, pulmonary haemorrhages, chronic conjunctivitis	Treat skin burns by the prescribed treatment (Table 40). As bromine
<b>Hydrocyanic acid</b>	R	As cyanogen compounds	As cyanogen compounds
<b>Hydrofluoric acid</b>	R and S	Irritation and etching of the mucous membranes and skin, the destructive action affects also the tissue under the skin and the blood vessels (painful bleeding), suppurating wounds which heal with difficulty. The acid gas is too pungent for voluntary inhalation. Inhalation is possible only when victim is trapped	Skin burns : as in hydrochloric acid. In hydrofluoric acid poisoning give calcium salts internally
<b>Hydrogen sulphide</b>	R and S	<i>Acute</i> : headache, inflammation of conjunctivae ; exposure to high concentration : pain of the eyes, inflammation of the mucous membranes, vomiting, cold sweats, colic, diarrhoea and dysuria, shortness of breath, coughing, palpitations, bronchitis or bronchopneumonia <i>Chronic</i> : inflammation of the eyes, bronchitis, headache, weakness, lassitude, digestive disturbances, loss of weight, general debility, jaundice, in some instances dermatitis	Respiratory failure : warm, complete rest, respiration therapy ; continue for several hours. Give coffee. Care of eyes, thoroughly flushing with water followed by the use of a saturated boric acid solution and olive oil. Pain can be controlled by local anaesthetics. Warm boric acid solution bandages against further complications

R—respiratory tract    S—skin    D—digestive tract

(Continued on next page)



Table 39—continued

Compound	Means of absorption	Toxic effects	First aid
<b>Lead and its compounds</b>	R and D	<i>Chronic</i> : the symptoms manifest themselves after a long time (cumulation); weakness, lassitude, loss of appetite, loss of weight, lead line on gums, pallor, followed in severe cases by colic, headache, pain about joints	See a doctor at once. Calcium injections and a suitable diet are the most useful treatments of chronic lead poisoning
<b>Manganese compounds</b>	R	Psychic and nervous disturbances	
<b>Mercury and its compounds</b>	R and D	<i>Acute</i> : metallic taste in mouth, nausea and vomiting, bloody diarrhoea, albumin in the urine, headache, rapid pulse, cramps, affections of the respiration tract, followed by swelling and bleeding of gums, sometimes a blue line of mercury sulphide on gums and lips, ulcers on cheeks and lips, swelling of the lymph and salivary glands In severe cases the teeth may become loose or may be expelled, following the development of abscesses <i>Chronic</i> : affection of the teeth, indigestion, anaemia, loss of weight, nervous disorders (trembling of fingers and hands, trouble in walking and speaking), headache, pain in the joints	See a doctor
<b>Methanol</b>	R and D	Irritation of the mucous membranes, headache, dizziness, shortness of breath, and especially damages of the nervous system, particularly the optic nerve (pain in the eyes, and partial or even permanent blindness)	Ingestion : emetics and gastric lavage with solution of sodium-bicarbonate (40 gm/l) Inhalation : correction of the acidosis is the most important phase (sodium bicarbonate)
<b>Nitrobenzene and other nitro-compounds of benzene and its homologues</b>	R, S and D	<i>Acute</i> : drowsiness, faintness, headache, and unsteadiness of gait (drunkenness), flushed face followed by cyanosis, irregular pulse, low blood pressure. In severe cases : marked cyanosis of lips and nailbeds, as well as pallor of the skin, dark blood and dark urine, weak and thready pulse, unconsciousness, death <i>Chronic</i> : pallor, anaemia, fatigue, headache, icterus, anorexia, somnolence	Remove contaminated clothing and wash the skin with soap. Complete rest. If swallowed, gastric lavage should be performed at once, and a large dose of magnesium sulphate or similar saline cathartic should be left in the stomach. No oily cathartic should be given Inhalation: in case of unconsciousness or severe methaemoglobin development oxygen should be administered. Stimulants (coffee)
<b>Nitrous fumes and nitric acid</b>	R	<i>Acute</i> : the symptoms are usually delayed; in non-fatal cases, headache, dizziness, cough, palpitation of the heart and sometimes cyanosis, restlessness, sleeplessness and pneumonia. The depressive action sometimes suppresses the cough reflex and obscures the danger <i>Chronic</i> : headache, sleeplessness, loss of appetite and weight, dyspepsia, constipation, and ulcers of the mucous membranes	Any individual suspected of having been exposed to nitrogen dioxide should be put to bed for 24 hours and given complete rest in a heated room. If necessary, oxygen. No stimulants

R—respiratory tract    S—skin    D—digestive tract

(Continued on next page)

Table 39—continued

Compound	Means of absorption	Toxic effects	First aid
<i>Petroleum Hydrocarbons</i>	R	Mental confusion, headache, dizziness	Fresh air, heat, complete rest. Remove saturated clothes. Artificial respiration if needed.
<i>Phenol</i>	R, D and S	Irritation of the skin and mucous membranes. Exposure of the skin gives severe white coloured burns unless the material is removed in a few minutes, extensive local erosions which heal slowly. Large exposure of the skin will lead to serious poisoning; headache, vertigo, nausea, dyspnea, excitement, convulsions, unconsciousness, respiratory paralysis <i>Chronic</i> : digestive disturbances, headache, vertigo, fainting, mental disturbances, nephritis, degeneration of liver	Burns: see Table 40. swallowing mustard or soapy water as emetic. Repeat emetic several times, then give large dose of epsom salts. Follow with syrup of lime and keep patient warm and quiet. Do not give oils. General methods: respiratory stimulants if necessary (5-7 per cent carbon dioxide in oxygen, coffee)
<i>Phosgene</i>	R	Tightness in chest, coughing, headache, violent pulmonary oedema. Phosgene has a dangerous delayed effect	Absolute rest, however well the patient feels. Keep him warm. Oxygen may be given. Do not use artificial respiration
<i>Selenium compounds</i>	R	Respiratory irritation, cough, garlic odour of the breath, oedema of the lungs, vomiting, diarrhoea, abdominal pain or cramps, loss of reflexes, cerebral irritation as manifested by convulsions and death	No specific treatment; diuretics, oxygen inhalations
<i>Sulphur dioxide</i>	R	<i>Acute</i> : irritation of the mucous membranes; low concentrations; sore throat, cough: higher concentrations; hoarseness, a sense of oppression and chest pain, difficulty in swallowing, bronchitis; very high concentrations: acute bronchitis, cyanosis, pulmonary oedema and death <i>Chronic</i> : chronic mild nasopharyngitis and chronic bronchitis, pallor, anorexia, bad taste, cough, inflamed eyes, reddened and shiny tongue	Eyes: see ammonia. Complete rest in a warm room. Artificial respiration if necessary, if respiration is difficult and pulmonary oedema is present pure oxygen should be administered. Combat acidosis with administration of sodium bicarbonate or sodium lactate

R—respiratory tract    S—skin    D—digestive tract

Table 40. First aid for chemical burns

<i>Compound</i>	<i>Treatment</i>
<i>Alkalis (potassium hydroxide, sodium hydroxide, ammonia, calcium oxide, sodium carbonate, potassium carbonate)</i>	Flush immediately with large quantities of water, then with a solution of acetic acid (20 gm/l)
<i>Alkali cyanide, hydrocyanic acid</i>	Wash with sodium permanganate, then rinse with ammonium sulphide
<i>Bromine</i>	Treat with a mixture of 1 vol ammonia (25 per cent) + 1 vol turpentine + 10 vol alcohol (96 per cent)
<i>Chromic acid</i>	Flush with water, then rinse with ammonium sulphide
<i>Hydrofluoric acid</i>	Flush with large quantities of cold water, next with a 50 gm/l solution of sodium bicarbonate and then apply a wet bandage with a paste of glycerol and magnesium oxide (2-1)
<i>Phosphorus</i>	No water. Treat the burns with a copper sulphate solution (10 gm/l)
<i>Phenol (carbolic acid)</i>	Flush with large quantities of water, then with a mixture of 4 vol alcohol (70 per cent) and 1 vol ferric chloride (1 N)
<i>Tar, pitch, tar oil</i>	Remove stains with cotton-wool soaked in xylene. Then apply lanolin
<i>Zinc chloride, silver nitrate</i>	Flush with water, then rinse with a solution of sodium bicarbonate
<i>Acids (sulphuric acid, hydrochloric acid, nitric acid, acetic acid, formic acid, oxalic acid, picric acid)</i>	Flush with large quantities of water, then with a saturated solution of sodium bicarbonate



Table 41. General principles of respiratory protective devices

<i>Type</i>	<i>Characteristics</i>	<i>Protection</i>
1 Atmosphere supplying apparatus	A hood or a mask separates the wearer from the surrounding atmosphere	Against severely contaminated atmosphere, provided it does not contain a substance which irritates or is absorbed by the skin
<i>a</i> Oxygen breathing apparatus	The oxygen is supplied from a cylinder provided with a pressure regulator, a breathing bag and an absorber of carbon dioxide. A mask excludes the surrounding atmosphere	The time during which the apparatus gives protection is limited by the capacity of the cylinder and of the carbon dioxide absorber
<i>b</i> Airline apparatus, hose mask	Supplies fresh air under a hood or a mask with the aid of a blower, or a source of compressed air	During an unlimited time and, combined with the hood, also against dusts and sprays
2 Air purifying respirators	The contaminated air is inhaled through a filter or canister. A mask separates the wearer from the surrounding atmosphere. An exhalation valve lowers the total resistance the wearer has to overcome in breathing through the apparatus and decreases the volume of the dead space of the system	Gives protection only in an atmosphere containing sufficient oxygen and on the condition that the concentration of the contaminant is low (for gases < 2 per cent by volume). The canister must contain the proper absorbent for the specific contaminant. The absorbent must still be active and the mask and filter or canister must not leak. The time of protection is limited

Table 42. Colour code for British gas mask canisters

No.	Type	Colour	Protection against
1† 6†	A C*	Blue Black	Ammonia Organic vapours <i>e.g.</i> acetone, amyl acetate, benzene, carbon disulphide, carbon tetrachloride, chloroform, dimethyl sulphate, diazomethane, ether, methanol, pentanol, petroleum, phenol, pyridine, toluene, tri-chlorethylene and arsine (specify : 'For arsine' on order)
7†	CC*	Black with grey stripe	For all gases under C plus fine smokes and dusts, and for : formaldehyde, aniline, acetaldehyde, acridine, acrolein, chloro-nitrobenzene
10†	CG	Red	Acid gases <i>e.g.</i> bromine, chlorine, phosgene, phosphine
11†	CGC	Red with grey stripe	For all gases under CG plus fine smokes and dusts, and for hydrobromic acid, hydrochloric acid, hydrofluoric acid, sulphur chloride, sulphuryl chloride
17† 20†	NF SH	Orange Red with white stripe	Nitrous fumes Hydrogen sulphide, sulphur dioxide
21†	SHC	Red with white and grey stripes	For gases under SH plus fine smokes and dusts and for sulphur trioxide and sulphur dioxide, produced by burning sulphur or pyrites
18†	O	Black with orange stripe	Methyl chloride
19†	P	Black with green stripe	Methyl bromide
5	B	Green	All service, carbon monoxide, nickel carbonyl
13 14 15	D H K	White Blue and black Red and white	Carbon dioxide and hydrocyanic acid Ammonia, nicotine and gases under C Highly acid gases associated with carbon dioxide
26	NFC	Orange with grey stripe	Nitrous fumes and other acid gases
2	ACC	Half blue, half black, grey line	Ammonia, organic vapours and smokes
3	ANF	Half blue, half orange	Ammonia and nitrous fumes

(Continued on next page)

Table 42—continued

No.	Type	Colour	Protection against
4	ANFC	Half blue, half orange, grey line	Ammonia, nitrous fumes and smokes
8	CDC	Black and white with grey line	Sulphur dioxide, sulphur trioxide and benzene
9	CD	Black and white	Sulphur dioxide and benzene
12	CGCE	Red with grey band	Chlorine and acetic anhydride
16	L	Half red, half orange	Acid gases and nitrous fumes
22	A (snout type)	Blue	Ammonia
23	CD (snout type)	Two thirds black one third white	Sulphur dioxide and benzene
24	CG (snout type)	Red	Acid gases
25	B	Green	All service and carbon monoxide (extra large)
27	E	Khaki	War gases
28	C (snout type)	Black	Organic vapours

\*The C and CC canisters should not be used for arsine if they are likely to be exposed to hydrocyanic acid. For such conditions a special canister can be supplied.

†The first ten types are approved by the Home Office for use under the Chemical Works Regulations

DAVIS, R. H. *Breathing in irrespirable atmospheres*, London, 1946



Table 43. Code and Composition of the German Gas mask Canisters

Type	Colour	Protection against	Absorbent	
			Auer	Draeger
A	Brown	Organic vapours	Activated carbon	
B	Grey	Acid gases	1 Activated carbon 2 Diatomite brick impregnated with potassium carbonate, hexamethylene tetramine and complex zinc salts	1 Activated carbon 2 Diatomite brick impregnated with alkali carbonate, hexamethylene tetramine and zinc salts
E	Yellow	Sulphur dioxide	Diatomite brick impregnated with alkali carbonate	
G	Blue	Hydrocyanic acid	Diatomite brick impregnated with	
			Complex salts	Amines
J	Blue and brown	Cyklon B (mixture of hydrocyanic acid and kieselguhr)	Combination of A and G	
K	Green	Ammonia	Diatomite brick or activated carbon impregnated with	
			Salts of heavy metals	Zinc salts
L	Yellow and red	Hydrogen sulphide	Metallic oxides	Manganese peroxide
M	Yellow and green	Hydrogen sulphide and ammonia	Activated carbon with a copper salt	
O	Grey and red	Phosphine and arsine	Activated carbon with metal oxides	
CO	Grey with a black band (3 cm)	Carbon monoxide	Hopcalite packed between layers of calcium chloride, calcium carbide serving to detect saturation of the calcium chloride (Auer)	

Table 44. Colour and letter code for gas mask canisters in the U.S.A.

<i>Letter</i>	<i>Colour</i>	<i>Protection against</i>
A	White*	Acid gases <i>e.g.</i> chlorine, formic acid, hydrochloric acid, hydrocyanic acid, hydrogen sulphide, phosgene and sulphur dioxide
B	Black*	Organic vapours <i>e.g.</i> acetone, alcohol, aniline, benzene, carbon disulphide, carbon tetrachloride, chloroform, ether, formaldehyde, petroleum and petroleum derivatives
C	Green	Ammonia
D	Blue	Carbon monoxide
AE, BE, <i>etc</i>	Half in contrasting black or white stripe on the respective colour	Dust, fumes, mists, fogs and smokes in combination with any of the above gases or vapours, acid gases and organic vapours
AB	Yellow	Acid gases and organic vapours
ABC	Brown	Acid gases, organic vapours and ammonia
N	Red	All of the above atmospheric contaminants

\*Canisters for a single gas or vapour other than ammonia or carbon monoxide are to have a 0.5 in coloured stripe around the canister near the bottom. The colour of the stripe will be assigned.

Table 45. Life of Puretha canisters (Siebe Gorman and Co., London) in an atmosphere containing 1 per cent by volume of the contaminant by an inspiration rate of 16 litres per minute

<i>Letter</i>	<i>Protects against</i>	<i>Contaminant</i>	<i>Maximum time of actual service min</i>	<i>Maximum absorption of contaminant gm</i>
CG	<i>Acid gases</i>	<i>Chlorine</i>	80—85	40
		<i>Phosgene</i>	75—80	17
		<i>Hydrochloric acid</i>	75	20
		<i>Sulphur dioxide</i>	18	8
		<i>Hydrogen sulphide</i>	20	5
C SH	<i>Organic vapour</i> <i>Hydrogen sulphide</i> <i>Sulphur dioxide</i>		50—100	—
			45	11
			60	28
A (contains 700cm <sup>3</sup> of a mixture containing about 40 per cent hydrated copper sulphate)	<i>Ammonia</i>	<i>Air with 2 per cent ammonia</i>	90	22
		<i>Air with 5 per cent ammonia</i>	30	—

Table 46a. Effects of mechanical-filter respirators (percentage of total number of retained particles)

Type	Mark	Diameter of particles $\mu$				Average
		15	15—5	5—1	1	
<i>Siebe Görman</i>						
<i>Gt. Britain ...</i>	<i>Mark IV</i>	100	100	100	97	99
<i>Mine Safety Appliances (USA)</i>	<i>Comfo*</i>	100	100	100	97	99
<i>Willson (USA) ...</i>	<i>400 L*</i>	100	100	99	95	98
<i>Brison (Belgium)</i>	<i>7 L</i>	100	100	97	88	95
<i>Brison ...</i>	<i>IV†</i>	100	99	78	47	73
<i>Brison ...</i>	<i>IV†</i>	100	98	76	43	70
<i>Willson ...</i>	<i>22†</i>	100	98	76	35	68
<i>Brison ...</i>	<i>II‡</i>	100	98	71	44	67

\*Approved by the Bureau of Mines

†With one layer of cotton-wool

‡With two layers of cotton-wool

Table 46b. Inhalation resistance of dust respirator (flow of air 20 litres per minute, air contains 320 milligrams of dust per cubic metre)

Type	Mark	Resistance in mm water		
		Initially	After 1 hr	After 2 hr
<i>Brison ...</i>	<i>7L</i>	1	1	1
<i>Willson ...</i>	<i>400 L Ad</i>	4	5	5
<i>Siebe Görman ...</i>	<i>Mark IV</i>	4	6	7
<i>Mine Safety Appliances ...</i>	<i>Comfo</i>	6	12	18
<i>Brison ...</i>	<i>IV</i>	2	11	24
<i>Brison ...</i>	<i>II</i>	2	28	60
<i>Willson ...</i>	<i>22</i>	5	38	78

SCHRENK, H. H. List of respiratory protective devices approved by the Bureau of Mines

BIDLOT, R. L'activité de l'Institut d'Hygiène des Mines au cours de l'année 1948 *Ann. Mines Belg.* 48 (1949) 242



Table 47. Common hazardous chemicals according to Committees of the National Fire Protection Association and American Chemical Society (1946)

Name	Normal packing	Life hazard	Fire hazard	Extinguisher	Storage : safety precautions
Acetic acid (glacial) $\text{CH}_3\text{COOH}$	Glass	Painful burns of skin, severe poison when swallowed	Vapour flammable (flash point $40^\circ\text{C}$ ). Dangerous in contact with chromic acid, sodium peroxide or nitric acid	Water	Isolate from oxidizing materials; expands on solidification ( $\text{m.pt } 16^\circ\text{C}$ )
Acetone $\text{CH}_3\text{COCH}_3$	Glass, steel	Slight narcotic action	Vapour flammable (flash point $-16^\circ\text{C}$ ). Explosive mixtures with air (2.6-12.8). Ignition temperature $538-566^\circ\text{C}$ . Vapour density 2	Water, carbon dioxide	Electrical equipment explosion proof. Automatic sprinkler systems or total flooding carbon dioxide system
Aluminium (dust) Al	Wood		Explosive mixtures with air may react violently with chlorinated hydrocarbons	Sand, do not use water or carbon tetrachloride	Keep dry
Ammonia $\text{NH}_3$	Glass, steel	Severe irritation of mucous membranes, flood of tears, blindness, caused by the vapour already in low concentrations	Vapour density 0.6, explosive ranges 15-26 per cent by volume	Water	Cool and in a fire-resistant room. Isolate from halogens and acids. Keep gasmask with proper canister at hand
Bromine $\text{Br}_2$	Glass, earthenjugs, surrounded by incombustible packing	Violent irritation of air passages and eyes, already in very low concentrations	Causes fire in contact with organic substances	Water	Store apart from other materials. Keep goggles and gasmask at hand
Calcium carbide $\text{CaC}_2$	Steel, tin coated steel		Gives off acetylene gas on contact with water or moisture	Sand, do not use water	Keep dry and apart from other materials in a fire-proof separate place
Calcium oxide $\text{CaO}$	Wood	Irritation of the skin and the eyes by the dust of calcium oxide	Develops heat upon contact with water or moisture and may cause ignition of organic material	Sand, do not use water	Keep dry
Carbon disulphide $\text{CS}_2$	Glass, earthenware, metal surrounded by incombustible packing	Very active nerve and systemic poison	Extremely flammable (flashpoint $-30^\circ\text{C}$ ). Explosive mixtures with air (1.50 per cent), the ignition temperature is dangerously low ( $100^\circ\text{C}$ ), the vapour can be ignited by a heavy blow, vapour density 2.6	Sand, carbon dioxide (self-contained breathing apparatus should be kept at hand)	Store cool in a fire-resistant room, if possible. Use explosion proof electric equipment under an inert gas. Never allow waste to be poured in the drain. Burn waste in a safe place

(Continued on next page)

<i>Name</i>	<i>Normal packing</i>	<i>Life hazard</i>	<i>Fire hazard</i>	<i>Extinguisher</i>	<i>Storage : safety precautions</i>
Chlorinated lime (bleaching powder, calcium hypochlorite) $\text{CaClOCl}$	Glass, wood, steel, tinned steel	Irritating action of chlorine gas	May cause fire when in contact with finely divided organic materials	Water, preferably spray. Keep gas-mask with canister at hand	Store cool and dry, isolate from acids and combustibles, use gas-mask with canister
Chlorine $\text{Cl}_2$	Steel cylinders	Very poisonous, severely irritating the eyes and mucous membranes and the respiratory organs even at very low concentrations	Violently chemically reactive with many common substances. May cause fire and explosion with ammonia	Keep self-contained breathing apparatus at hand	Isolate and cool ; gasmask with canister or self-contained breathing apparatus should be used
Ether (ethyl) $(\text{C}_2\text{H}_5)_2\text{O}$	Glass, tin, steel	Anaesthetic	Highly volatile, vapour flammable (flash point $-45^\circ\text{C}$ ) ; explosive range 2-37 per cent, ignition temperature $180^\circ\text{C}$ , vapour density 2.6 ; on standing and especially on exposure to sunlight it forms very explosive peroxides	Carbon dioxide, sand, carbon tetrachloride	Isolate in a cool fire-resistant room, electrical equipment must be explosion-proof ; add active carbon to prevent formation of peroxide ; test for presence of peroxide before using
Formic acid $\text{HCOOH}$	Glass	Corrosive	Flammable ; explosive mixtures with air		
Hydrochloric acid $\text{HCl}$	Glass, rubber lined steel	Severely irritating on eyes, mucous membranes and respiratory tract, extremely corrosive	Not combustible in air ; evolution of hydrogen in contact with metals ; this hydrogen may contain arsine	Water	Well ventilated storeroom, isolate from oxidizing agents, particularly nitric acid and chlorates
Hydrofluoric acid $\text{HF}$	Lead, paraffin or gutta percha lined bottles	Extremely corrosive and very poisonous ; causes skin burns and affects the eyes and respiratory tract	Strongly oxidizing liquid, may cause ignition of combustible material and may decompose violently if contaminated with most metals or their salts	Water	Isolate, ventilate ; use gloves and goggles
Hydrogen peroxide (27.5 per cent by weight) $\text{H}_2\text{O}_2$	Glass, aluminium (all containers must be vented)	Irritation of eyes, skin and lungs	Very combustible, powder with air, explosive, liberation of hydrogen in contact with water and with acids. Reacts with halogenated hydrocarbons.		Cool place ; in ventilated containers, isolated from combustible material and catalytic metals (iron, copper, chromium), use goggles and gloves
Magnesium $\text{Mg}$	Metal			Dry graphite, sand. Do not use water, carbon tetrachloride or carbon dioxide	Isolate and dry in a fire-resistant storeroom

(Continued on next page)

Table 47—continued

Name	Normal packing	Life hazard	Fire hazard	Extinguisher	Storage : safety precautions
Nitric acid $\text{HNO}_3$	Glass	Extremely poisonous and corrosive	Fire risk with combustible materials		Isolate in ventilated storeroom ; keep gasmask with canister at hand
Phenol $\text{C}_6\text{H}_5\text{OH}$	Hermetically sealed tin cans protected by wooden boxes	Extremely poisonous, easily penetrates the skin	Yields flammable vapours (flash point $78^\circ \text{C}$ )		Never store with food
Phosphorus, red $\text{P}$	Hermetically sealed cans	Yields toxic fumes when burning	Flammable ; explosive when mixed with oxidizing materials	Water followed by wet sand	Isolate from chemicals
Phosphorus white or yellow $\text{P}$	Under water in hermetically sealed cans	Extremely poisonous ; contact with the skin causes severe burns ; yields highly toxic fumes when burning	Highly flammable ; explosive in contact with oxidizing material ; ignites spontaneously on contact with air	Water followed by wet sand	Isolate in fire-resistant storeroom ; store large quantities under water ; do not handle it with the fingers
Potassium $\text{K}$	Under petroleum, in glass, tin, steel ; hermetically sealed	Dangerous on skin, strong caustic action	Ignites spontaneously on exposure to air ; with water violent reaction (fire phenomena and spattering)	Dry graphite, sand or dry loose soda ash	Store dry ; keep bottle in metal container ; destroy waste personally ; use goggles
Potassium cyanide $\text{KCN}$	Glass, earthenware, metal ; hermetically sealed	Very poisonous			Isolate, avoid contact with acids or moisture ; deteriorates in unsealed bottle
Potassium hydroxide $\text{KOH}$			As calcium oxide		
Potassium sulphide $\text{K}_2\text{S}$	Iron, glass	Corrosion of the skin ; evolves hydrogen sulphide on contact with air			Avoid contact with acid ; deteriorates in unsealed bottle
Silver nitrate $\text{AgNO}_3$	Amber or black coloured glass	Corrosive and poisonous	Has oxidizing properties		Store in dark, cool place ; keep away from combustible material

(Continued on next page)



Table 47—continued

Name	Normal packing	Life hazard	Fire hazard	Extinguisher	Storage: safety precautions
Sodium Na					
Sodium cyanide NaCN					
Sodium hydroxide NaOH					
Sulphur S	Wood	When burning forms sulphur dioxide, a poisonous gas that irritates the respiratory tract	Flammable; the dust forms explosive mixtures with air; hazardous in contact with oxidizing materials	Water	Isolate from oxidizing materials in a ventilated storeroom
Sulphuric acid H <sub>2</sub> SO <sub>4</sub>	Glass, iron	Corrosive and irritating fumes; liquid produces burns	May cause ignition on contact with combustible materials	Sand, do not use water	In ventilated storerooms, avoid contact with: metals, oxidizing materials and combustible materials; corrosive, use gloves, goggles
Zinc (powder) Zn	Paper, wood	The fumes of zinc are very poisonous	Evolves hydrogen in contact with acids or with strong alkalis; sometimes also with water; dust may form explosive mixtures with air; may react violently with chlorinated hydrocarbons	Sand, do not use water or carbon tetrachloride	Dry, ventilated place away from water and moisture; isolate from acids

Oxidizing materials: chlorates, perchlorates, bromates, nitrates, nitrites, peroxides, permanganates, chromium trioxide cause fire hazard, especially in the presence of combustible materials. They can be extinguished with water, except the peroxides on which sand should be used.

Store cool and dry in a fire-resistant room and isolated from combustible materials and acids.

Table 48. Transmittances and tolerances in transmittance of Filter Lenses

Operations	U.S.A.			Great Britain			Germany			Netherlands		
	$L^*$	$I_{total}$	$U$ 0.365 $\mu$	$L$	$I_{total}$	$U$ 0.32- 0.35 $\mu$	$L^*$	$I$ 0.95 $\mu$	$U$ 0.35 $\mu$	$L$	$I$ 1 $\mu$	$U$ 0.365 $\mu$
Gas cutting, medium gas welding ...	0.45- 1.18	1.5	0.1	0.1- 1.0	0.1	0.1	0.06- 0.3	0.13	12.6	0.2- 0.8	1	1.0
Heavy gas welding, arc welding and cutting (30-75 amp) ...	0.061- 0.164	1.0	0.1	0.01- 0.1	0.03	0.01	0.06- 0.3	0.0048	1.6	0.04- 0.2	0.3	0.3
Arc welding and cutting (75-200 amp)	0.0085- 0.023	0.6	0.1	0.001- 0.01	0.003	0.001	0.001- 0.06	0.0048	1.6	0.01- 0.04	0.3	0.3
Arc welding and cutting (200-400 amp)	0.0012- 0.0032	0.5	0.05	0.001- 0.01	0.003	0.001	0.001- 0.06	0.00017	0.004	0.002- 0.01	0.1	0.1

$L$ : Percentage luminous transmittance (lamp 2,800 °K)

$I$ : Percentage maximum infra-red transmittance (wavelength about 1  $\mu$ )

$U$ : Percentage maximum ultraviolet transmittance (wavelength about 0.35  $\mu$ )

RUTGERS, G. A. W. Beschermingsglazen voor lasarbeid *Veiligheid* 24 (1948) 114

STAIR, R. Spectral-transmissive properties and use of eye-protective glasses *Nat. Bureau Stand. Washington Circ.* 471, 1948

British Standard Specification 679 : 1936

German standards DIN 4646 (1933) and DIN 4647 (1937)

Standards for eye-protection *Nederlandse Stichting voor Verlichtingskunde* N952, Arnhem, 1948

Table 49. Percentage transmittances and tolerances in transmittance of various shades of filter lenses in the U.S.A.

Shade-number	Maximum infra-red transmittance	Maximum spectral transmittance in the ultraviolet and violet			
		313 $m\mu$	334 $m\mu$	365 $m\mu$	405 $m\mu$
1.5	25	0.2	0.8	25	65
1.7	20	0.2	0.7	20	50
2.0	15	0.2	0.5	14	35
2.5	12	0.2	0.3	5	15
3.0	9.0	0.2	0.2	0.5	6
4.0	5.0	0.2	0.2	0.5	1.0
5.0	2.5	0.2	0.2	0.2	0.5
6.0	1.5	0.1	0.1	0.1	0.5
7.0	1.3	0.1	0.1	0.1	0.5
8.0	1.0	0.1	0.1	0.1	0.5
9.0	0.8	0.1	0.1	0.1	0.5
10.0	0.6	0.1	0.1	0.1	0.5
11.0	0.5	0.05	0.05	0.05	0.1
12.0	0.5	0.05	0.05	0.05	0.1
13.0	0.4	0.05	0.05	0.05	0.1
14.0	0.3	0.05	0.05	0.05	0.1

STAIR, R. Spectral Transmissive properties and use of eye protective glasses  
*Nat. Bur. Stand. Circ.* 471, 1948



Table 50. British standard identification colours for gas cylinders

Gas	Colour	
	Cylinder	Band
Acetylene ... ..	Maroon	—
Air ... ..	Grey	—
Ammonia ... ..	Black	Red and yellow
Argon ... ..	Blue	—
Carbon dioxide (for temperate use) ...	Black	—
Carbon dioxide (for tropical use) ...	Black	White or aluminium Black bottom
Carbon dioxide (medical) ... ..	Green	—
Carbon dioxide (with internal tube for making snow)... ..	Green	—
Carbon monoxide ... ..	Red	Yellow
Chlorine ... ..	Yellow	—
Coal gas ... ..	Red	—
Ethyl chloride (flammable) ... ..	Grey	Red
Ethyl chloride (non-flammable) ... ..	Grey	—
Ethylene ... ..	Mauve	Red
Ethylene oxide ... ..	Mauve	Red and yellow
'Freon' (dichlorodifluoromethane) ...	Bottom end grey	Neck end mauve
Helium ... ..	Medium brown	—
Hydrocyanic acid ... ..	Blue	Yellow
Hydrogen ... ..	Red	—
Methane ... ..	Red	—
Methyl bromide ... ..	Blue	Black
Methyl chloride (flammable) ... ..	Green	Red
Methyl chloride (non-flammable) ... ..	Green	—
Neon ... ..	Medium brown	Black
Nitrogen ... ..	Grey or dark grey	Black
Nitrous oxide (for medical use) ...	Black	—
Oxygen ... ..	Black	—
Oxygen (for medical use) ... ..	Black	White
Oxygen and carbon dioxide mixture (for medical use) ... ..	Black	Green, white neck
Phosgene ... ..	Black	Blue and yellow
Sulphur dioxide ... ..	Green	Yellow
Gases not listed above :		
Non-combustible and non-poisonous	} Aluminium	Yellow
Non-combustible and poisonous ...		Red
Combustible and non-poisonous		Red and yellow
Combustible and poisonous ...		

(The principles underlying the system of marking are that yellow should represent toxic or poisonous gases and red or maroon those which are flammable)

British Standard Specification 349 : 1932

Table 51. Identification of gas cylinders at the Staatsmijnen in Limburg (Netherlands)

Gas	Markings on the cylinders			
	Colour of band and cap	Name	(CO !) on the coloured band	Skull
Acetylene ... ..	Yellow	Acetyleen	No	No
Ammonia ... ..	Grey	Ammoniak	No	No
Carbon dioxide ... ..	Grey	Koolzuur	No	No
Carbon monoxide ... ..	Grey	Koolmonoxyde	Yes	Yes
Chlorine ... ..	Grey	Chloor	No	Yes
Coke oven gas ... ..	Red	Cokes oven gas	Yes	Yes
Ethylene ... ..	Red	Aethyleen-fractie	Yes	Yes
Hydrogen ... ..	Red	Waterstof	No	No
Methane ... ..	Red	Motormethaan	Yes	Yes
Nitrogen ... ..	Green	Stikstof	No	No
Oxygen ... ..	Blue	Zuurstof	No	No
Sulphur dioxide ... ..	Grey	Zwaveldioxyde	No	Yes

Table 52. Scheme for the identification of Piping Systems American Standard Association

Classifi- cation	Equipment and contents of pipes	Colour (entirely or in bands)
F	Fire protection materials and equipment : sprinkler systems and other fire fighting equipment	Red
D	Dangerous materials : flammable, cor- rosive, explosive or poisonous material	Yellow or orange
S	Safe materials : (products involving no hazard in their handling and having no extraordinarily high value)	Green (or the achro- matic colours, white, black, grey or alumi- nium)
P	Protective materials : (gases or liquids used as antidotes to poisonous and cor- rosive materials)	Bright blue
V	Extra valuable materials (otherwise safe materials, but which have very high value)	Deep purple

It is also advisable to identify the pipes by lettering the name of material on the pipe

Table 53. Identification of pipe lines in Germany

<i>Contents of pipes</i>	<i>Colour</i>	
	<i>Pipe</i>	<i>Band</i>
Steam : saturated ... ..	Red	—
superheated ... ..		White
waste ... ..		Green
Water : drinking ... ..	Green Green Green Orange Black	—
hot ... ..		White
under pressure ... ..		Red
salt ... ..		—
impure ... ..		—
Air : cold ... ..	Blue	—
hot ... ..		White
compressed ... ..		Red
mixed with coal dust ... ..		Black
Gas : blast furnace (crude) ... ..	Yellow	Black
blast furnace (purified) ... ..		—
generator gas ... ..		Blue
town gas ... ..		Red
acetylene gas ... ..		White
water gas ... ..		Green
oil gas ... ..		Brown
Acids : ... ..	Orange	—
concentrated ... ..		Red
Caustic lye : ... ..	Lilac	—
concentrated ... ..		Red
Oil : ... ..	Brown	—
gas oil ... ..		Yellow
tar oil ... ..		Black
Tar ... ..	Black	—
Vacuum ... ..	Grey	—



Table 54. Determination of noxious contaminants in the air

Contaminant	Absorbing agent	Reagents	Reaction	Method
Acetaldehyde <chem>CH3CHO</chem>	Water	Schiff's reagent : acid solution of fuchsin and <chem>NaHSO3</chem>	Violet red colour	Colorimetric
Acetone <chem>CH3COCH3</chem>	Silica gel	—	Adsorption	Gravimetric
Acids	1 N NaOH	0.1 N iodine, 0.1 N <chem>Na2S2O3</chem> , starch indicator	Formation of iodoform	Iodometric
Acrolein <chem>CH2 : CHCHO</chem>	0.1 N NaOH		Neutralization	Titrimetric
	Water or ethanol	Schiff's reagent	Violet red colour	Colorimetric
	Ethanol	Benzidine acetate	Yellow colour	Colorimetric
Ammonia <chem>NH3</chem>	1 N sulphuric acid	Nessler's reagent	Yellow colour	Colorimetric
	Moist litmus paper	Turns blue after t sec	ppm	
		t = 70 6.5 1	1 10 100 1,000	
		instantaneously		
Amyl acetate and other esters	Water, alkali, alcohol or combinations of these		Hydrolysis	Titration of the excess NaOH
	0.1 N sulphuric acid (remove organic dust by filtration)	Solution of bromine indicator, 0.2 per cent indigo disulphonate	Formation of tribromaniline	Titrimetric
Aniline <chem>C6H5NH2</chem>	0.5 N hydrochloric acid	Add 2 drops hypochlorite reagent (50 gm calcium hypochlorite) and after 5 min 5 ml phenol reagent (5 gm phenol in 1 litre N ammonia)	Formation of a deep blue coloured dye	Colorimetrically with toluidine blue standards, checked with a copper sulphate potassium permanganate solution
Arsenic As	Solution of alkali hydroxide	Nascent hydrogen	Reduction to arsine	Iodometric (cf arsine)
Arsine <chem>AsH3</chem>	Solution of KI in dilute <chem>H2SO4</chem>		Liberation of iodine	Iodometric
	Mercuric chloride paper		Yellow brown → black stain	Colorimetric
	Solution of bromine or NaOBr	Ammonium molybdate	Blue colour after reduction	Colorimetric

(Continued on next page)

Table 54—continued

Contaminant	Absorbing agent	Reagents	Reaction	Method
Benzene $C_6H_6$	Concentrated $H_2SO_4$ and formaldehyde		Brown colour	Colorimetric
	Absorb in mixture of fuming nitric acid (1.5) and sulphuric acid (1.84) extract m-dinitrobenzene with methylethylketone		Formation of m-dinitrobenzene characterized by yellow colour	Colorimetric
	Nitrating acid	Titanous chloride, after separation of the m-dinitrobenzene by steam distillation	Reduction of the m-dinitrobenzene with excess of standard titanous chloride	Titration of excess titanous chloride with ferric alum
		Hydrogen peroxide	Conversion to bromide	As AgBr, gravimetric or colorimetric
Bromine $Br_2$	Solution of alkali hydroxide	Chlorine water and a solution of fuchsin in 0.1 N $H_2SO_4$ extract with isoamyl alcohol	Violet colour	Colorimetric
	Solution of potassium iodide		Liberation of iodine	Iodometric titrimetric
Carbon dioxide $CO_2$	After drying with $CaCl_2$ absorb in soda-lime or ascarite		Formation of carbonate	Gravimetric
	1 N barium hydroxide			Titration of excess $Ba(OH)_2$
Carbon disulphide $CS_2$	Alcoholic solution of copper sulphate to which is added a solution of diethylamine in benzene		Formation of the orange coloured copper diethyldithiocarbamate	Colorimetric determination of diethyldithiocarbamate
	Solution of potassium hydroxide in alcohol	Faintly acid cupric acetate solution and acetic acid till acid on litmus paper	Formation of potassium xanthate which is precipitated as copper xanthate	Colorimetric or titrimetric with iodine solution
	Combustion followed by absorption and estimation of the sulphur dioxide		—	Electrical conductivity of the solution
Carbon monoxide $CO$	Mice or canaries (unreliable)		—	Rapid poisoning
	Suspension of iodine pentoxide in oleum (for concentrations higher than 0.1 per cent CO)		Oxidation of CO to $CO_2$ with liberation of iodine	Measure the decrease in volume
	Palladium chloride test paper		Brownish yellow to black stain	Colorimetric (colour chart)
	Silicagel impregnated with a silica molybdenum compound and palladium sulphate as a catalyst		Green colour	Colorimetric (colour scale)

(Continued on next page)

Contaminant	Absorbing agent	Reagents	Reaction	Method
Carbon monoxide CO (continued)	Pumice impregnated with a suspension of iodine pentoxide in oleum		Green colour	Colorimetric (colour chart)
	Pass over iodine pentoxide at 100° C and absorb iodine in a solution of KI		Oxidation	Titration of the iodine or determination of the CO <sub>2</sub>
	Pass over red mercuric oxide at 175-200° C, determine the mercury vapour with selenium sulphide paper		Reduction of HgO black stain of test paper	Colorimetric (colour chart)
	By complete combustion on a hot platinum wire		Oxidation	Estimation of the CO <sub>2</sub> or the heat effect
	Pass over hopcalite or similar catalyst		Oxidation	Estimation of the CO <sub>2</sub> or the heat effect
Chlorinated organic compounds	Blood	Pyrotannic acid	Formation of carmine suspension	Colorimetric (colour chart)
	Dilute solution of blood or of haemoglobin (completely reduced with Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> )		Characteristics of absorption spectrum	Determination of the volume of sample to be passed to split the absorption band (spectroscope)
	Silica gel		Adsorption	Gravimetric
	Flame test with alcohol flame and copper wire		Green blue flame colour	Colorimetric
	Pass over hot platinum wire and absorb reaction product in water		Formation of HCl	Titrimetric
Chlorine Cl <sub>2</sub>	Dilute solution of potassium iodide		Liberation of iodine	Titrimetric with sodium thiosulphate
	Water	Acidified benzidine hydrochloride solution	Blue colour	Colorimetric (permanent copper-sulphate picric acid standards)
		Acidified o-tolidine solution	Yellow colour	Colorimetric
	Test paper with copper and benzidine acetates		Blue colour	Colorimetric (colour chart)
	Test paper with methyl orange and mercuric chloride		Pink colour	Colorimetric (colour chart)
Hydrogen cyanide HCN	Test paper with copper sulphate, guajac and methyl orange		Blue colour	Colorimetric
	Solution of sodium bicarbonate and a known quantity of iodine, starch added as the indicator		Formation of cyanogen iodide	Volumetric (pass sample through solution till blue colour has disappeared)

(Continued on next page)



Table 54—continued

Contaminant	Absorbing agent	Reagents	Reaction	Method
<i>Hydrogen cyanide</i> HCN (continued)	Dilute alkali hydroxide solution	Add ferrous sulphate, acidify and then add ferric chloride	Formation of prussian blue	Colorimetric
		Boil with ammonium polysulphide, acidify and add ferric chloride	Formation of thiocyanate	Colorimetric
<i>Hydrogen fluoride</i> HF	Dilute alkali hydroxide solution	Acidify; add a solution of zincium nitrate and 1, 2, 5, 7-tetrahydroxy anthraquinone (quinizarin)	Formation of a coloured lake	Colorimetric
		Acidify and distil	—	Titrimetric with thorium nitrate
<i>Hydrogen sulphide</i> H <sub>2</sub> S	Test paper with lead acetate		Formation of PbS, brown black stain	Colorimetric (photoelectric)
	Silver cyanide on activated alumina		Formation of Ag <sub>2</sub> S stain (grey)	Length of stain is a measure of the H <sub>2</sub> S content
	Solution of cadmium acetate	Add iodine and acid	Reduction of iodine	Iodometric titration of excess iodine
	Test paper with selenium sulphide		Black stain	Colour scale
<i>Mercury</i> Hg	Absorption of ultraviolet light (wavelength 2,537 Å) radiated by a mercury lamp			Photoelectric
	Trap vapour in a tube chilled by liquid air	Electrolysis of the solution of the mercury in chlorine water		Measure diameter of mercury drop (microscope)
		Dissolve the mercury in chlorine water and extract with chloroform solution of dithizone	Green → orange yellow	Colorimetric
<i>Lead</i> Pb	Concentration: a impinger for dust, b electric precipitation for fumes c filtration: dissolve concentrate in dilute nitric acid	H <sub>2</sub> S	Formation of sulphide, black stain	Colorimetric
		K <sub>2</sub> CrO <sub>4</sub>	Formation of lead chromate	Gravimetric or iodometric
		Ammoniacal cyanide solution of dithizone, extract with chloroform	Red	Colorimetric
		—	—	Polarographic

(Continued on next page)

Contaminant	Absorbing agent	Reagents	Reaction	Method
Nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$	Water	Reduce with zinc and hydrochloric acid to aniline, then react with hypochlorite, phenol and ammonia	Blue colour	Colorimetric
	Nitrating acid	Extract the m-dinitrobenzene with methylethylketone	Yellow colour	Colorimetric
	Water or dilute solution of alkali hydroxide	Solution of sulphanilic acid, $\alpha$ -naphthylamine and acetic acid	Rose pink	Colorimetric
Nitrogen peroxide $\text{NO}_2$		After oxidation with hydrogen peroxide add phenoldisulphonic acid or salicylic acid	Formation of coloured nitration product	Colorimetric
	Silica gel	React with diphenylamine sulphuric acid	Blue	Colorimetric
	Water or solution of alkali hydroxide	Solution of mercury in nitric acid (Millon's reagent)	Red	Colorimetric
Phosgene $\text{COCl}_2$	Testpaper with diphenylamine and	p-dimethylaminobenzaldehyde	Yellow or orange stain	Colorimetric (colour chart)
	Standard solution of sodium hydroxide in alcohol		Hydrolysis	Titration of excess NaOH
	0.1 N sodium bicarbonate		Hydrolysis	Titration of chloride ion
Sulphur dioxide $\text{SO}_2$	Saturated aqueous solution of aniline		Diphenyl urea precipitates	Gravimetric
	0.01 N solution of iodine in potassium iodide 10 gm/l		Reduction of iodine	Titration of excess iodine
	Dilute solution of hydrogen peroxide		Formation of $\text{H}_2\text{SO}_4$	Titration
Trinitrotoluene $\text{C}_6\text{H}_2\text{CH}_3(\text{NO}_2)_3$	Aqueous solution of manganous sulphate 0.3 gm/l	Potassium iodide and potassium iodate	Formation of $\text{H}_2\text{SO}_4$	Iodometric titration
	Testpaper with potassium iodide or iodate, starch and glycerol		Blue	Colorimetric
	Isopropyl alcohol	After reduction with titanous chloride, the amine is diazotized with dimethyl-1-naphthylamine		Colorimetric

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Table 55. Methods of sampling air contaminants

<i>Apparatus</i>	<i>Air l/min</i>	<i>Absorption reagent</i>	<i>Contaminants</i>
<i>Washing bottle with glass filter inlet</i>	0.5—1	0.1—1.0 N NaOH	<i>Acetic acid, acetone, bromine, esters, formaldehyde, hydro- chloric acid, hydrocyanic acid, hydrofluoric acid, nitric acid, sulphur dioxide</i>
		0.02—0.1 N HCl or H <sub>2</sub> SO <sub>4</sub>	<i>Alkalis, ammonia, aniline and other amines</i>
		<i>Bromine water</i>	<i>Phosphine</i>
		<i>Cadmium acetate</i>	<i>Hydrogen sulphide</i>
<i>Impinger</i>	30	<i>Water</i>	<i>Ammonium salts, arsenic compounds, lead compounds</i>
		0.1 N NaOH	<i>Chromic acid</i>
		0.5 N HNO <sub>3</sub>	<i>Lead, lead compounds</i>
	2.8	<i>Diethylamine ethanol</i>	<i>Trinitrotoluene</i>
<i>Glass bead column</i>	1	<i>Nitrating acid</i>	<i>Nitrobenzene, benzene</i>
<i>Electrostatic precipitator</i>	80	—	<i>Arsenic compounds</i>



Table 56. Methods of sampling by concentration of a chemical contaminant of the atmosphere

Contaminant	Absorp- tion method	Absorbent	Rate of flow of air, l/min
Acetaldehyde ...	2 W	Water	1
Acids ... ..	W	0.1 N NaOH	1
Acetone ... ..	2 W	1 N NaOH	1
Acrolein ... ..	W	Water or ethyl alcohol	1
Alkali mists ...	W	0.02 N HCl	1
Ammonia ... ..	W	0.02 N acid	1
Ammonium salts ...	m.i.	Water	3
Aniline (homologues)	2 W	0.1 N H <sub>2</sub> SO <sub>4</sub>	0.5
Arsenic compounds	e	—	80
	i	Water or alkali	30
Arsine ... ..	W	Solution of KI in dilute H <sub>2</sub> SO <sub>4</sub>	0.5
Benzene ... ..	W	Nitrating acid	0.05
	W	Conc. H <sub>2</sub> SO <sub>4</sub> and formal- dehyde	1
Bromine ... ..	W	0.1 N NaOH	1
Carbon dioxide ...	2 W	0.1 N Ba (OH) <sub>2</sub>	0.5
Carbon disulphide...	W	0.1 N alcoholic KOH	0.5
Chlorine ... ..	2 W	KI (100 gm/l)	1
Chromic acid ...	i	0.1 N NaOH	30
Esters ... ..	2 W	Water, alkali, alcohol or combinations of these	1
Formaldehyde ...	W	0.1 N NaOH	1
Hydrogen cyanide	W	0.1 N KOH	1
Hydrogen fluoride	W	0.1 N KOH	1
Hydrogen sulphide	W	Cadmium acetate 20 gm/l	1
Nitrobenzene ...	W	Water	0.5
	b	Nitrating acid	0.05
Nitrogen oxides ...	W	1 N KOH and H <sub>2</sub> O <sub>2</sub> (30 gm/l) 7 + 1	0.15
Phenol ... ..	3 W	Water	0.5
Phosgene ... ..	2 W	0.1 N NaHCO <sub>3</sub>	1
Phosphine ... ..	2 W	Bromine Water	0.5
Sulphur dioxide ...	W	0.1 N NaOH	1
Trinitrotoluene ...	m.i.	Diethylaminoethanol	3.0

W=wash bottle with glass filter inlet  
b=column with glass beads  
i=impinger  
m.i.=midget impinger  
e=electrostatic precipitator

Table 57. Effect of different substances on platinum

Action of molten substances		Attack by chemicals at temperatures over 800°C	
Substance	Minimum temp °C at which attack becomes manifest	Substance	Effect
NaOH ... ..	500	$\text{HPO}_3$ : $(\text{NH}_4)_2\text{HPO}_4$	Attacked by formation of a platinum subphosphide with 3.8 per cent phosphorus (eutectic at 588°C)
KOH ... ..	400		
$\text{Ba}(\text{OH})_2$ ... ..	400		
$\text{NaNO}_3$ ; $\text{KNO}_3$ ... ..	800		
$\text{Ba}(\text{NO}_3)_2$ ... ..	700	$\text{KPO}_3$ ; $\text{KH}_2\text{PO}_4$	Only in the presence of free carbon
$\text{NaOH}$ ; $\text{K}_2\text{CO}_3$ (covered crucible)	900		
$\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$ (2:1)	700	$\text{K}_2\text{HPO}_4$ ; $\text{K}_4\text{P}_2\text{O}_7$ $\text{K}_3\text{PO}_4$ ; $\text{Ca}_3(\text{PO}_4)_2$	Immediate attack No effect
$\text{NaOH}$ and $\text{Na}_2\text{O}_2$ (13:7)...	500		
$\text{NaCN}$ ; $\text{KCN}$ ... ..	900	$\text{MgHPO}_4$	Slight attack
$\text{NaOH}$ and $\text{NaCN}$ ... ..	500	$\text{Mg}_2\text{NH}_4\text{PO}_4$ ; $\text{Mg}_2\text{P}_2\text{O}_7$	No effect
$\text{KOH}$ and $\text{K}_2\text{S}$ (open crucible)	500	$\text{Mg}(\text{PO}_3)$ $\text{Mg}_2\text{As}_2\text{O}_7$	Violent attack Detrimental over 920°C, no effect in a current of oxygen
$\text{KOH}$ and $\text{K}_2\text{S}$ (closed crucible, reducing) ... ..	800		
$\text{NaCl}$ ; $\text{KCl}$ ... ..	750—850	$\text{SiO}_2$ Blue core of burner flame	No effect Generally hazardous
$\text{Na}_2\text{SO}_4$ ; $\text{K}_2\text{SO}_4$ ... ..	900—1,200		

Table 58. Comparison of Filter Papers

No.	Trade name					Grade	Characteristics
	Durieux	Delta	Schleicher and Schüll	Whatman	Machery, Nagel and Co.		
1	Violet	Violet Black 369 368	— 590	— 44	640 dd	Fine	Used for
2	Blue	Green 367	Blue 589 <sup>3</sup>	Red 42	640 d		Fine precipitates, ash-free
3	White	Brown 366	White 589 <sup>2</sup>	White 40	640 m		Fine precipitates, ash content very low
4	Green	— 111	Yellow 589 <sup>4</sup>	Green 43	—	Normal	Normal precipitates
5	Red	Blue 365	Black 589 <sup>1</sup>	Blue 41	640 w		As No. 3, extra free from grease
6	'Durcis'	— 128	— 575	— 50	—	Coarse	Gelatinous precipitates
7	Black	— 375	— 375	— 31	—		Corrosive solutions (alkalis, acids) Coarse precipitates



## APPENDIX

### BRITISH LEGAL REQUIREMENTS

Although not every laboratory can be regarded as part of a Factory, as defined in Section 151 of the Factories Act 1937, the following Acts and Regulations have a direct bearing on the use of chemicals, and may be applicable.

Factories Acts 1937 and 1948 and Acts to be read as one with them

Petroleum (Consolidation) Act 1928

Explosives Act 1875

Public Health (Smoke Abatement) Act 1926

Alkali *etc* Works Regulation Act 1906

Casting of Brass S.R. and O. 1908 No. 484

Bronzing S.R. and O. 1912 No. 361

Celluloid Regulations S.R. and O. 1921 No. 1825

Cellulose Solutions S.R. and O. 1934 No. 990

Chemical Works S.R. and O. 1922 No. 731

Chromium Plating S.R. and O. 1931 No. 455

Electric Accumulator Regulations S.R. and O. 1925 No. 28

Enamelling of metal or glass S.R. and O. 1908 No. 1258

Indiarubber S.R. and O. 1922 No. 329

Lead Compounds S.R. and O. 1921 No. 1443

Luminising S.R. and O. 1947 No. 865

Two-Bath Chrome Tanning S.R. and O. 1918 No. 368

This list cannot be regarded as in any way exhaustive, but it includes the major requirements which are likely to be met.

## MEANING OF SOME MEDICAL TERMS

*Agranulocytosis*—Disease of the blood showing a gradual and progressing diminution of the number of granulated white cells.

*Allergic reactions*—General reactions of the organism caused by contact with a substance which by the first contact with the body (and that may have been far in the past) has given rise to a state of extreme sensitivity called allergy.

*Alveolus (pl. alveoli)*—The fine air sacs of the lungs where the exchange of oxygen, carbon dioxide and other gases between the air and the blood takes place.

*Anaemia*—A deficiency in the blood and in its constituents especially in the haemoglobin content.

*Antidote*—A drug administered to counteract the effects of a poison.

*Arterial blood*—Oxidized blood.

*Arteries*—Blood vessels conducting blood from the heart to the body-tissues.

*Blood plasma*—Liquid in which blood cells are dispersed.

*Capillaries*—The thinnest blood vessels connecting the arteries with the veins.

*Carcinogenic substance*—Substance causing cancer if inhaled, swallowed or coming in contact with the skin.

*Coma*—A state of deep unconsciousness.

*Cornea*—The horny transparent membrane which forms the anterior portion of the eye ball.

*Conjunctivitis*—Inflammation of the conjunctivae.

*Conjunctiva*—The mucous membrane which lines the inner surface of the eyelids and the front of the eye.

*Cyanosis*—Bluish colour of the skin and mucous membranes, caused by a deficiency in oxyhaemoglobin of the blood in the peripheral blood vessels.

*Dermatitis*—Irritation (inflammation) of the upper layers of the skin.

*Dyspnoea*—Tightness of the chest, difficult breathing.

*Erythroblasts*—The mother cells of the red blood cells.

*Granulomatosis*—Cell growth with formation of granules.

*Heart centre*—Group of cells within the nervous system governing the function of the heart muscles.

*Haemoglobin*—The pigment of the red blood cells.

*Haemoglobinuria*—After haemolysis, the haemoglobin is excreted by the kidneys and appears in the urine.

*Haemolysis*—The blood cells are disintegrated and the haemoglobin is dissolved in the plasma.

*Hypodermic injection*—Subcutaneous injection.

*Keratitis*—Inflammation (often with ulceration) of the horny coat of the eye.

*Lachrymatory substance*—Tear exciting substance.

*Lung fibrosis*—A diffuse growth of connective tissue between the air sacs of the lungs, thereby obstructing the ventilation of the lungs.

*Maximal breathing capacity*—The maximal amount of air that passes through the lungs in one minute while breathing at a maximal rate and depth.

## MEANING OF SOME MEDICAL TERMS

*Myelocytes*—The mother cells of the granulated white blood corpuscles.

*Necrosis*—Death of a group of tissue cells.

*Nephritis*—Inflammation of the kidneys.

*Oedema*—A swelling due to the effusion of plasma from the blood into the intercellular spaces of a tissue.

*Pneumokoniosis*—Dust disease of the lungs.

*Pneumonia*—Inflammation of the lungs.

*Pneumococci*—Bacteria which cause one form of pneumonia.

*Respiration centre*—Group of cells within the nervous system governing the respiration (rate and depth).

*Shock and collapse*—Situations wherein the harmonious collaboration between the organs of the human body, especially between blood circulation, respiration and heat regulation, has ceased owing to some disintegrating influence.

*Thrombosis*—The obstruction of a blood vessel through the formation of a clot or thrombus within its walls.

*Veins*—Blood vessels conducting blood from the body tissues to the heart.

*Venous blood*—Reduced blood.



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